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# Functionalized Benzazines as Luminescent Materials and Components for Optoelectronics

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## Abstract

Extensive research on the synthesis and application of benzazine derivatives for electronic devices, luminescent elements, photoelectric conversion elements, and image sensors has been published recently. In the frames of this review article data obtained within the period 2012–2018 on the synthesis and optical properties of functionalized quinolines, quinoxalines and quinazolines are considered. Arylvinyl-, arylethynyl- and (het)aryl derivatives of these benzazines, their photoluminescence and photoisomerisation are discussed. Examples of photosensitive annelated, oligo- and polymeric benzazines and also coordination compounds with benzazine ligands are reviewed.

Bibliography 267 references.

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## I. Introduction

Organic photosensitive materials have attracted much attention during the past two decades due to their applications in electronic and optoelectronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic solar cells (OSCs), sensors and many others, as indicated by numerous publications, including recent monographs.<sup>1-5</sup> In themed issue of Journal of Materials Chemistry dedicated to novel organic optoelectronic materials<sup>6</sup> it is noted that the research and development of these materials belong to the cross-disciplinary science

uniting chemistry, physics, materials science, electronics, nanotechnology and biology. Numerous reviews are devoted to separate aspects in the field of creation and use of new photosensitive materials. So, researches of luminescent materials, including organic, for semiconductor lighting have been presented in recent review article.<sup>7</sup> Authors of work<sup>8</sup> analyzed organic electroluminescent materials, including metalloorganic and coordination compounds, and also the devices radiating in UV and IR ranges. Data on coordination compounds of lanthanides with the organic ligands applied in design of electroluminescent diodes are systematized in another work of the same group of authors.<sup>9</sup> Recent advances in creation of the white light-emitting diodes (WOLEDs) having a number of advantages are presented.<sup>10,11</sup> New design of WOLEDs which allows to decrease the number of photolithographic cycles and to reduce the production cost is discussed in work.<sup>12</sup> Materials for highly effective phosphorescent OLEDs with low working voltage are described in the review.<sup>13</sup> Organic materials with nonlinear optical properties are presented.<sup>14</sup> Fundamental processes in organic photo cells are discussed.<sup>15</sup> Data on the physical mechanisms defining optoelectronic properties of high-performance organic materials, materials for organic solar cells and semiconductors are summarized.<sup>16</sup>

Organic compounds with expanded  $\pi$ -electronic system represent the basis of photosensitive materials. Among them the important place is taken by the structures including the electron donating and electron withdrawing groups connected through  $\pi$ -conjugated spacer, so-called push-pull systems. Molecular properties of such chromophores are defined by the ability of both donating and withdrawing fragments to participate in intramolecular charge transfer (ICT). Aromatic nitrogen-containing  $\pi$ -deficient heterocycles, such as pyridine, quinoline and their aza-analogs, are widely used as electron withdrawing part in the systems with ICT.<sup>13</sup> The ability of these heterocycles to protonation and complexation at nitrogen atoms, as well as incorporation of groups capable to polymerization expands the application of such compounds for the creation of light sensitive materials.<sup>10</sup>

Six-membered heterocycles with two nitrogen atoms – diazines (pyridazine, pyrimidine and pyrazine) and their benzoanalogs (quinazoline and quinoxaline) have already proved to be the key structural fragments in functionalized  $\pi$ -conjugated systems, and they are presented in a number of reviews.<sup>17-22</sup> Aryl, arylvinyl and arylolefin derivatives of pyrimidines and coordination compounds based on them are most studied, optical, electrochemical properties, photoluminescence, scopes of application are discussed.<sup>17-19</sup> As for similar derivatives of quinoxaline and quinazoline, some data are provided in reviews<sup>19,20,22,23</sup>, mainly such compounds are described in articles and patents. Taking into account that intensive researches of organic compounds as key components for OLEDs have begun with derivatives of quinoline,<sup>24</sup> which properties are close to quinoxaline and

quinazoline, it was of interest to carry out the comparative analysis of derivatives of these three heterocycles. Other benzo(di)azines such as isoquinoline, cinnoline and phthalazine have been much less used in the field of chromophores for optoelectronic.

In the present review we tried to summarize the data on the synthesis and optical properties of functionalized benzazines (quinolines, quinoxalines and quinazolines) as luminescent materials and components of optoelectronic devices. This review focuses on arylvinyl- arylethynyl- and aryl(hetaryl)benzazines, their metal complexes, annulated derivatives as well as oligomer and polymer structures bearing these moieties for the period of 2012–2018. Non aromatic benzazinones and structures bearing extra cycles will not be discussed here.

The following abbreviations are used in the current review:

AACC –activation/ alkynylation/ cyclocondensation,

acac – acetylacetonate,

AIE –aggregation-induced emission,

Alq<sub>3</sub> – complex of aluminium with 8-hydroxyquinoline,

BAZnP – butylaminozirconium phosphate,

biimquin – bis(imidazol-1-yl)quinoxaline,

bpy – 2,2-bipyridine,

Bz – benzoyl,

bzq – benzo[*h*]quinoline,

cd – candela,

CPDT – cyclopentadithiophene,

CPL – circularly polarized luminescence,

Cy – cyclohexyl,

D–A–D – donor–acceptor–donor,

dbm – dibenzoylmethane,

DBU – 1,8-diazabicyclo[5.4.0]undec-7-ene,

dca – dicyanamide,

DCM– dichloromethane,

dfppy – difluorophenylpyridine,

DFT –density functional theory,

dmp – дипивалоилметан;

DNA – deoxyribonucleic acid,

DPEPO – [bis(2-diphenylphosphoryl)]phenyl ester

dpquin – dipyrdo[3,2-*f*:2,3-*h*]quinoxaline,

dpquin(COOH)<sub>2</sub> – 6,7-dicarboxypyrdo[3,2-*f*:2,3-*h*]quinoxaline,

DSSC – dye-sensitized solar cell,  
 EFISH –electric field induced second harmonic,  
 ESIPT – excited state intramolecular proton transfer,  
 EQE –external quantum efficiency,  
 FRET –Förster resonance energy transfer,  
 FTO – fluorine-doped tin oxide,  
 GM – units of Goeppert-Mayer, characterizing two-photon absorption ( $1\text{GM} = 1 \cdot 10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ )  
 HEPES – 4-(2-hydroxyethyl)-1-piperazine-ethanesulphonic acid,  
 hip – deprotonated 5-hydroxyisophthalic acid,  
 HOMO – highest occupied molecular orbital,  
 H<sub>2</sub>qldc – quinolin-2,3-dicarboxylic acid,  
 3-Hqlc – quinolin-3-carboxylic acid,  
 ICT – intramolecular charge transfer,  
<sup>3</sup>MLCT –triplet metal-to-ligand charge transfer,  
<sup>3</sup>LC – triplet ligand-centred,  
 LLCT – ligand-ligand charge transfer,  
 LUMO – lowest unoccupied molecular orbital,  
 MTPP-Br – methyltriphenylphosphonium bromide,  
 MW – microwave irradiation,  
 Naph – naphthyl,  
 NLO – non-linear optics,  
 OFET – organic field-effect transistor,  
 OLED – organic light-emitting diode,  
 OPV – organic photovoltaics,  
 OSC – organic solar cell,  
 OTFT – organic thin film transistor,  
 ITO – indium tin oxide,  
 P3HT – poly(3-hexylthiophene),  
 PBS – sodium phosphate buffer,  
 PCE – power conversion efficiency,  
 PEDOT – poly(3,4-ethylenedioxythiophene),  
 phen – 1,10-phenanthroline,  
 PhOLED – phosphorescent light-emitting diode,  
 PMMA – polymethylmetacrylate,

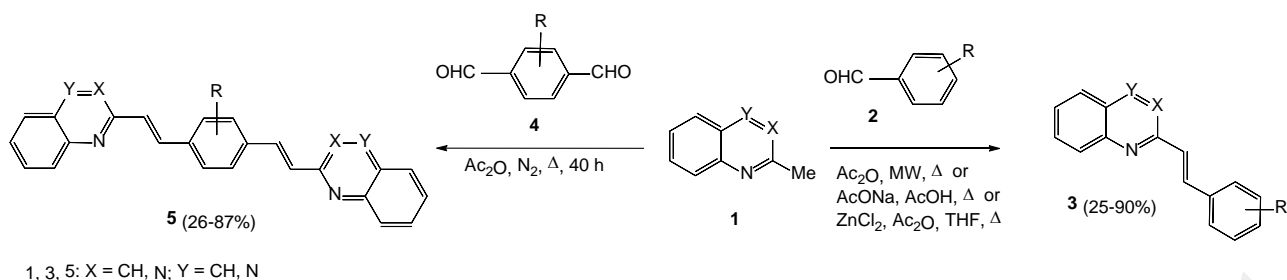
PPI – pyrophosphate,  
 ppq1 – 2,4-diphenylquinoline,  
 PSC – polymer solar cell,  
 PSS – polystyrolsulphonate,  
 Py – pyridyl,  
 PVC – photovoltaic cell,  
 q – 8-hydroxyquinoline,  
 ql – quinolone,  
 qnz – quinazoline,  
 qox – quinolin-*N*-oxide,  
 quin – quinoxaline,  
 RISC – reverse intersystem crossing,  
 rt – room temperature,  
 SMM – single molecule magnet,  
 TADF – thermally activated delayed fluorescence,  
 TCE – 1,1,1-trichloroethane,  
 TDDFT – time-dependent DFT,  
 Th – thienyl,  
 TFA – trifluoroacetic acid,  
 TIPS – triisopropylsilyl,  
 TMS – trimethylsilyl,  
 TPA –two-photon absorption,  
 TPEF – two-photon-excited fluorescence,  
 Vs – volatile solids,  
 WOLED –white organic light-emitting diode,  
 $\Phi_F$  – luminescence quantum yield.

## II. Arylvinyl-, arylethynyl- and (het)arylbenzazines

### II.1. Synthesis, photoluminescence and photoisomerization of arylvinylbenzazines

Condensation of 2-methylsubstituted benzazines **1** with arylcarboxaldehydes **2** or arylcarboxdialdehydes **4** under basic or acidic conditions represent traditional, synthetic approaches to arylvinylbenzazines **3**, **5** (Scheme 1).<sup>22</sup>

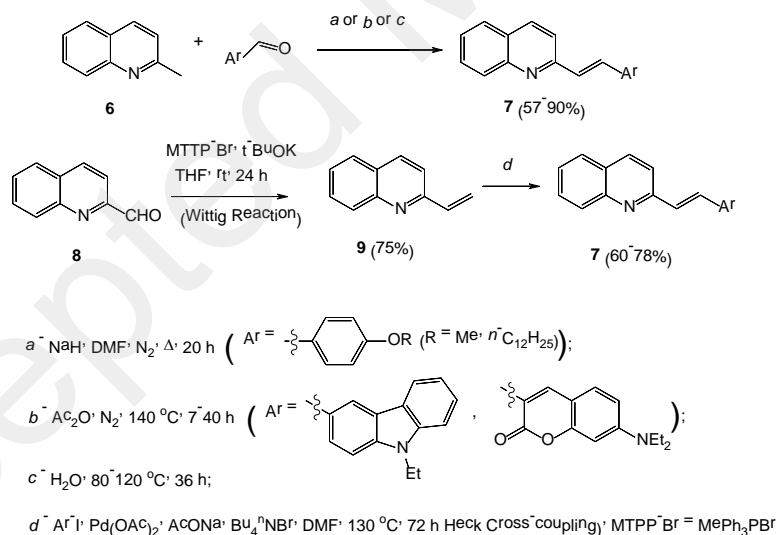
**Scheme 1**



### II.1.1. Arylvinylquinolines

2-Arylvinylquinoline chromophores are generally obtained exclusively as their *E* stereoisomer. Most of the time, they are obtained by functionalization of already formed quinoline fragment. 2-Arylvinylquinoline derivatives **7** can be easily prepared by condensation of arylcarboxaldehydes and 2-methylquinoline derivatives (**6**) (Scheme 2, top reaction). This reaction can be performed either in basic media,<sup>25</sup> in acetic anhydride<sup>26-28</sup> or even in water without the presence of any catalyst.<sup>29</sup> These derivatives can be also obtained in two steps from 2-quinolinecarboxaldehyde (**8**) (Scheme 2, bottom reaction).<sup>30</sup> The first step consists in a Wittig reaction with methyltriphenylphosphonium bromide to obtain 2-vinylquinoline **9**. This intermediate can be involved in a palladium catalyzed Heck cross-coupling reaction with aryl iodides to yield (*E*)-2-arylvinylquinolines **7**.

**Scheme 2**

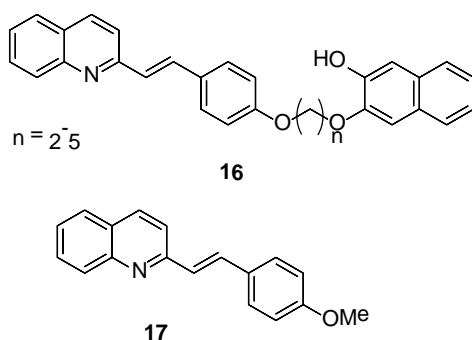


2-Styrylquinoline derivatives **12** can be also obtained from *ortho*-iodo anilines **10** and 2-*trans*-styryl propargyl alcohols **11** by domino synthesis initiated by a Sonogashira coupling and concluded by a base catalyzed propargyl alcohol-enone isomerization (Scheme 3, top reaction).<sup>31</sup> Suzuki cross coupling reaction with styrylboronic acids on 6,8-dibromo-4-chloroquinoline derivative **13** affords 4,6,8-tristyrylquinoline chromophores **14** (Scheme 3, bottom reaction).<sup>32</sup>

**Scheme 3**

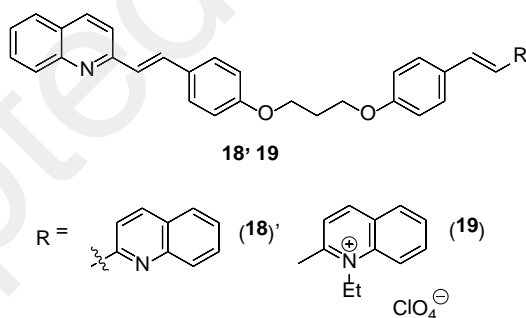




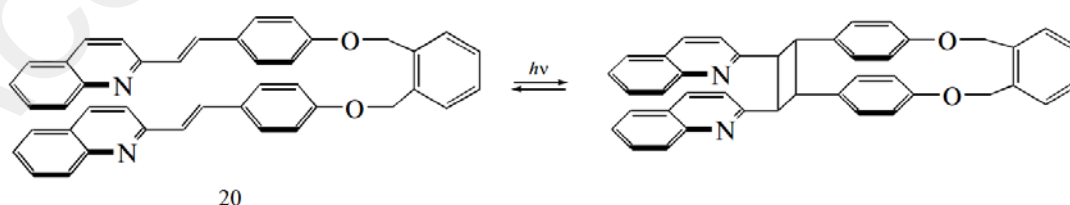


The same team<sup>39</sup> has designed also a monochromophoric dyad **18** bearing two 2-styrylquinoline fragments leading to **19** possible isomers: *EE*, *EZ*, *ZE* and *ZZ*. When the polyethylene linker incorporate an *o*-xylylene bridge (compound **20**), along with photoisomerization, [2+2]-photocycloaddition occurs affording tetrasubstituted cyclobutane (Scheme 5).<sup>40</sup> When one of the two 2-styrylquinoline is replaced by a styrylquinolinium fragment (dyad **19**),<sup>41-43</sup> photoisomerization of the styrylquinoline fragment occurs only on one-way: it goes in *cis*→*trans* direction whereas *trans*→*cis* isomerization is quenched because of competing FRET to the styrylquinolinium fragment. Nevertheless, *trans*→*cis* photoisomerization can be observed upon protonation of the styrylquinoline fragment. Therefore, the cycle protonation → *trans*–*cis* photoisomerization (reversible) → deprotonation → *cis*–*trans* photoisomerization (one-way) – can be repeated and used for design of controlled molecular photoswitches.

### Structures 18, 19

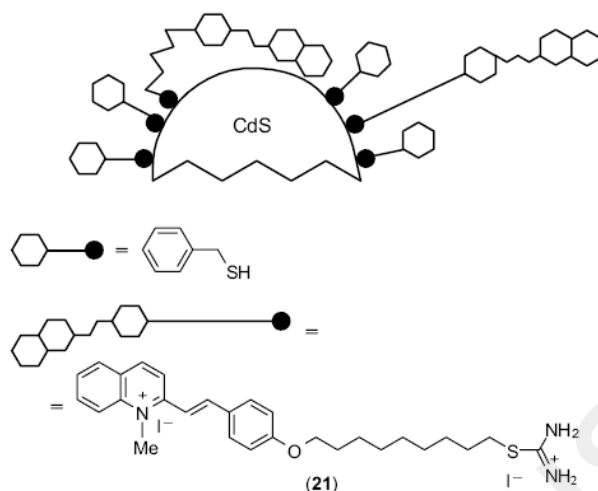


### Scheme 5



The particular attention was paid to heterogeneous catalysis when styrylquinolinium fragment has been grafted on quantum dot via isothiuronium anchor (compound **21**, Figure 1).<sup>44,45</sup>

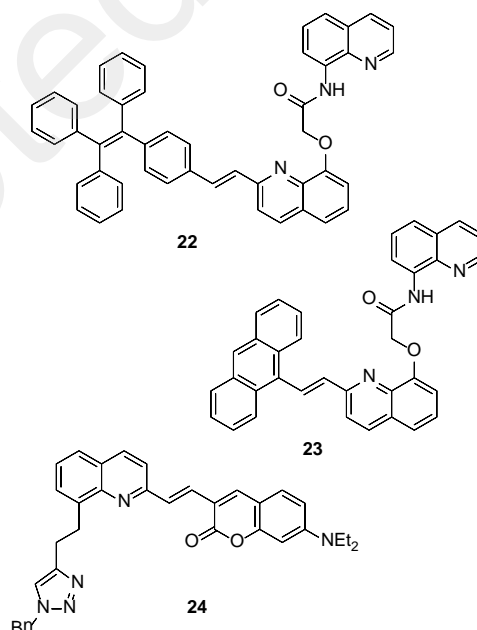
Compared to the free fragment, *E-Z* photoisomerization of the styrylquinolinium fragment grafted on quantum dot was suppressed and its photodestruction was accelerated.



**Figure 1.** Styrylquinoline **21** grafted on quantum dot.<sup>45</sup>

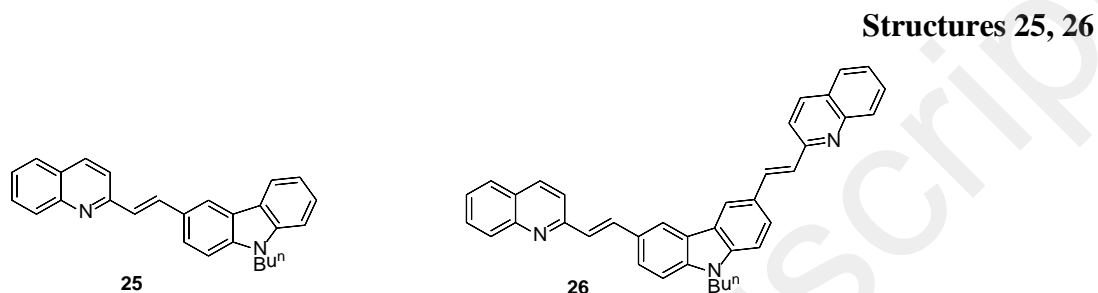
Xiong and coworkers have designed two styrylquinoline chromophores **22** and **23** bearing tetraphenylethene and anthracene fragments.<sup>26</sup> These compounds, nearly non emissive in DMSO/water system with low water content ( $f_w < 30\%$ ), exhibit aggregation induced emission (AIE). These compounds have been used as selective fluorescent probes of  $\text{Cu}^{2+}$  in aqueous solution and test strips (ON-OFF probe).

#### Structures 22-24

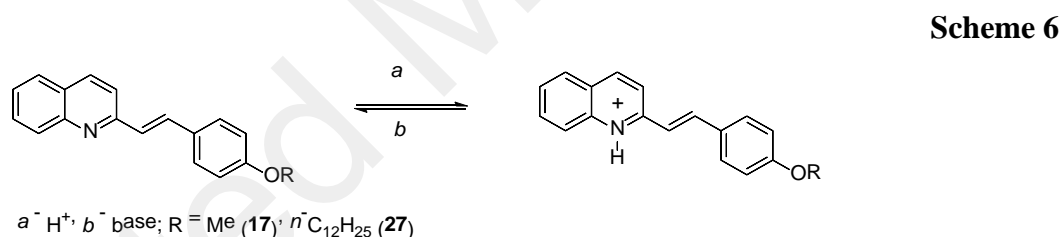


Wu and coworkers have designed a styrylquinoline chromophore **24** bearing a coumarin fragment.<sup>46</sup> This compound exhibits an emission at 516 nm in MeCN/water mixture and was used as selective ratiometric probe for  $\text{Zn}^{2+}$  in living cells.

Li and coworkers have designed carbazole derivatives **25** and **26**.<sup>28</sup> These compounds exhibit two-photon absorption in DMF solution (**25**:  $\sigma_{\text{TPA}} = 81 \text{ GM}$ , **26**:  $\sigma_{\text{TPA}} = 364 \text{ GM}$  measured by the two-photon excitation fluorescence (TPEF) method) and in doped polymethylmethacrylate (PMMA) thin film (**25**:  $\sigma_{\text{TPA}} = 470 \text{ GM}$ , **26**:  $\sigma_{\text{TPA}} = 621 \text{ GM}$  measured by the Z-Scan method).<sup>47</sup> Three-dimensional optical data storage experiments have been performed proving that these chromophores are well-suited as high-density optical information storage.

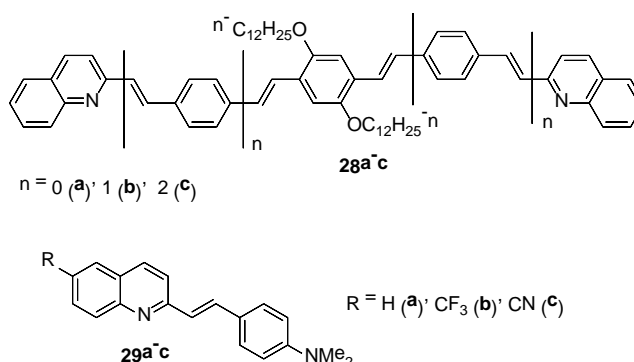


Yuang and coworkers have reported the solid state emission of alkoxy substituted styrylquinoline derivatives **17** and **27** (Scheme 6).<sup>25</sup> These compounds remain emissive upon reversible protonation with a remarkable red-shift ( $\lambda_{\text{em}} = 570\text{--}574 \text{ nm}$ ). Whereas the neutral forms exhibit negligible emission change upon mechanical force, remarkable piezochromism is observed for the protonated chromophores.



Flores-Noria and coworkers have designed phenylenevinylenequinoline derivatives **28a-c**. These compounds are highly luminescent in  $\text{CHCl}_3$ , THF and toluene.<sup>30</sup> A push-pull effect is only observed for compound **28a**, whereas for **28b** and **28c** no significant effects of the quinoline fragment are observed neither spectroscopically, electrochemically nor theoretically. Compound **28a** is the most emissive (in  $\text{CHCl}_3$   $\lambda_{\text{em}} = 499 \text{ nm}$   $\Phi_{\text{F}} = 0.64$ ) making it suitable for optoelectronic devices.

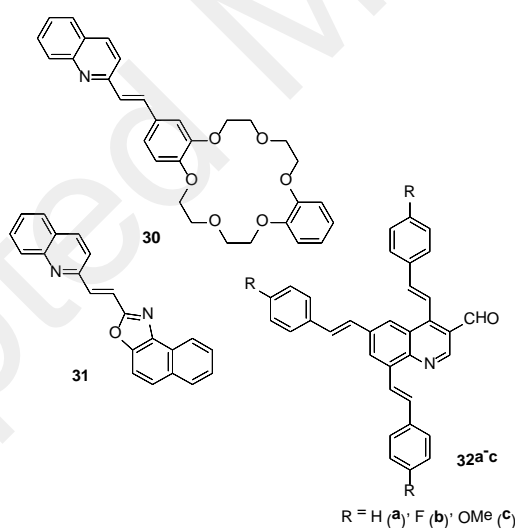
**Structures 28, 29**



Cinar *et al* have designed dimethylamino substituted styrylquinoline chromophores **29a-c**. In addition to strong emission solvatochromism characteristic of push-pull luminophores, these compounds exhibit a pH-sensitivity and "ON-OFF-ON" emission profiles.<sup>31</sup> Indeed the emission of these compounds can be quenched by addition of one proton (protonation of the quinoline ring) and blue shifted with respect of the free base upon a second protonation (amino group).

Tzeli and coworkers have designed theoretically a styrylquinoline derivative **30** bearing a benzo-18-crown-6-ether fragment.<sup>48</sup> Due to the reversible sensitivity of photophysical properties (absorption and emission) to the presence of  $H^+$ ,  $Ca^{2+}$  and the possibility of reversible photoisomerization, the author suggest the use of this chromophore to build logic gates.

#### Structures 30-32



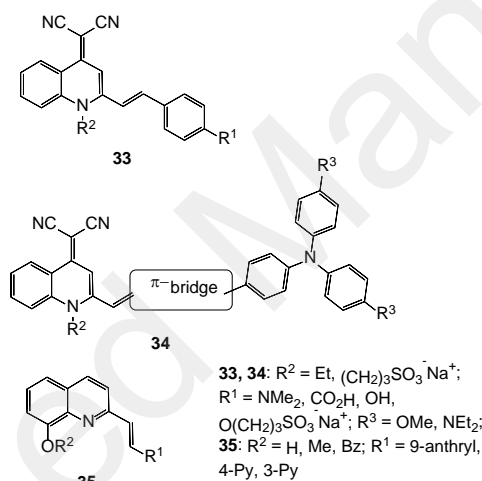
Zanocco *et al* have designed chromophore **31**. This compound exhibits intense white light emission based on proton transfer in solvent mixture including at least a strong hydrogen-bonding solvent such as MeOH (for 17% of DMSO, the chromacity coordinates are 0.33, 0.35 and quantum yield is 0.31).<sup>49</sup>

Mphahlele *et al* have designed 4,6,8-tristyrylquinoline derivatives **32a-c**.<sup>32</sup> Whereas chromophore **32a** exhibits yellow-green luminescence ( $\lambda_{em} = 529$  nm,  $\Phi_F = 0.06$ ) in DCM solutions, the substitution by electron-donating fluorine or methoxy group leads to blue shifted

emission with enhanced quantum yield (**32b**:  $\lambda_{\text{em}} = 420, 430 \text{ nm}$ ,  $\Phi_{\text{F}} = 0.17$  and **32c**:  $\lambda_{\text{em}} = 370, 470 \text{ nm}$ ,  $\Phi_{\text{F}} = 0.21$ ).

Styrylquinolines **33** and **34** with expanded  $\pi$ -electronic system, bearing quinolin-malonodinitryl as new building block were synthesized and studied as fluorophores with aggregation-induced emission (AIE) in red and near IR ranges.<sup>50</sup> Authors summarized recent advances and discussed potential application of such derivatives containing donating groups as agents for optical biovisualisation *in vivo*. Incorporation of different substituents ( $R$ ,  $R^1$ ,  $R^2$ ), including sulphonate groups, allows to apply compounds **33**, **34** both for preparation of AIE-active nanoparticles, and for drug delivery using nanoparticles. New strategy of molecular design for generation of nanoaggregates of different forms of these compounds possessing longwave emission was presented.

### Structures 33-35



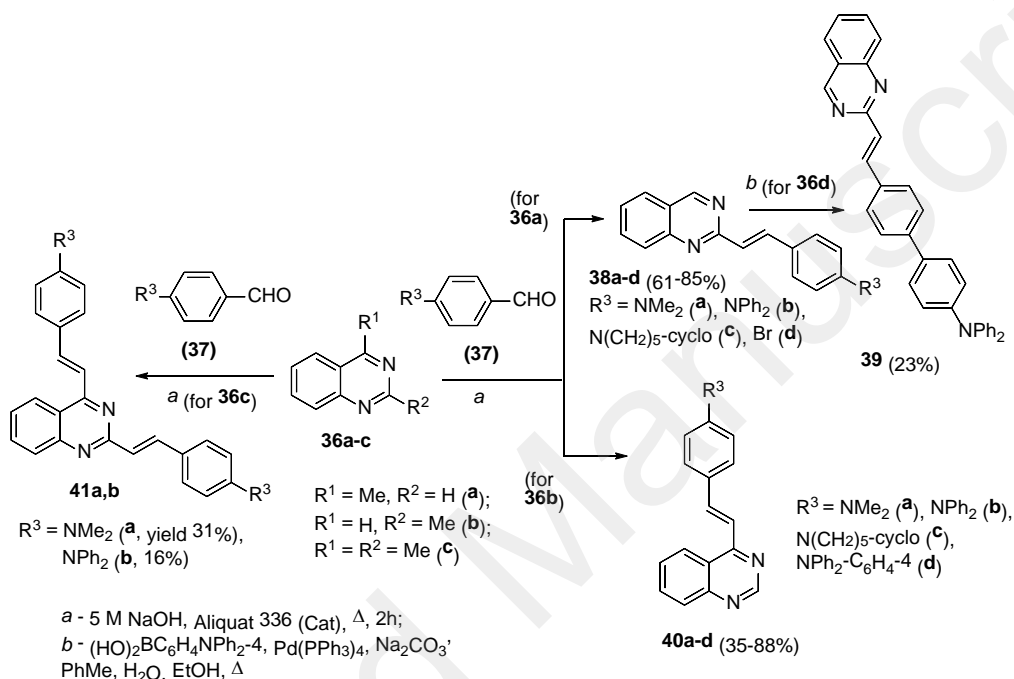
In continuation of research on 8-hydroxyquinoline derivatives the synthesis and photoluminescence of styrylquinolines **35**, bearing ether groups at position 8 of quinoline unit and anthracene or pyridine fragments ( $R^1$ ) was described.<sup>51-53</sup> It was shown that substitution of phenol hydrogen with methoxy group leads to the increase in fluorescence quantum yield from 0.067 to 0.25 for **35** ( $R^1 = 9\text{-anthryl}$ ), to 0.41 for **35** ( $R^1 = 4\text{-Py}$ ) and to 0.37 for **35** ( $R^1 = 3\text{-Py}$ ).

### II.1.2. Arylvinylquinazolines

Only few examples of arylvinylquinazoline chromophores have been described so far in the literature. 2- and 4-Arylvinylquinazolines **38a-d** and **40a-d** as well as 2,4-diarylvinylquinazoline **41a,b** can be obtained by Knoevenagel condensation from the corresponding methylquinazoline and benzaldehyde derivative exclusively as *E* isomers (Scheme 7).<sup>54</sup> The reaction can be performed with electron-donating substituted benzaldehyde and it should be noted that 4-bromobenzaldehyde reacts

only with 2-methylquinazoline. Bromo derivative **38d** can be involved in a Suzuki cross coupling reaction to obtain biphenylenevinylene derivative **39**. The methylquinazoline intermediates **36** are not commercially available but can be obtained either from chloro derivatives by palladium catalyzed coupling with trimethylaluminium (4-methylquinazoline (**36b**) and 2,4-dichloroquinazoline (**36c**))<sup>55</sup> or by cyclization reaction from 2-bromobenzaldehyde and acetamidine hydrochloride (2-methylquinazoline (**36a**)).<sup>56</sup>

Scheme 7

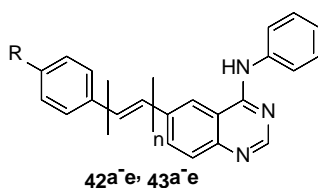


2-Arylvinylquinazolines **38a-c** and **39** exhibit green emission in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{\text{em}}$  = 520–545 nm), diphenylamino derivatives exhibit the highest fluorescence quantum yield (**38b**:  $\Phi_{\text{F}}$  = 0.61, **39**:  $\Phi_{\text{F}}$  = 0.65). It should be noted that biphenylenevinylene derivative **39** shows a significantly increased Stokes shifts ( $\Delta\nu$  = 7796 cm<sup>-1</sup>) with regard to its phenylenevinylene analogue **38**. 4-Arylvinylquinazoline analogues **40a-d** exhibit significantly red-shifted emission ( $\lambda_{\text{em}}$  = 548–610 nm) but reduced quantum yield (up to 0.25 for **40b**). 4,6-Diarylvinylquinazolines **41a,b** exhibit red-shifted emission maxima with regard to their 2-arylvinylquinazoline analogues but blue-shifted in comparison with their 4-arylvinylquinazoline analogues but with low emission quantum yield ( $\Phi_{\text{F}}$  = 0.02–0.09). All of these compounds exhibits strong emission solvatochromism, halochromism and are potential NLOphores.

Dhuguru and coworkers have described 6-arylvinyl- and 6-arylbutadienylquinazoline chromophores **42a-e** and **43a-e** obtained by Heck cross coupling reaction from 6-iodoquinazoline precursors.<sup>57</sup> Bromopyridines were involved into Suzuki cross-coupling reaction for the arylalkenylation of cycle.<sup>58</sup> All the compounds are luminescent in CHCl<sub>3</sub> with good to moderate

quantum yield ( $\Phi_F = 0.02$ – $0.57$ ). In the arylvinylquinazoline series **42a-e**, the most red shifted absorption and emission are observed for the dimethylamino derivative **42a** ( $\lambda_{\text{abs}} = 381$  nm and  $\lambda_{\text{em}} = 495$  nm) and the nitro chromophore **42e** ( $\lambda_{\text{abs}} = 372$  nm and  $\lambda_{\text{em}} = 539$  nm). A red shift in absorption and emission is observed for butadiene derivatives **43a-e** with regards to their vinyl analogues **42a-e**. For all these compounds emission is attributed to ICT (from electron donating group to the quinazoline fragment in case of **42a-c** and **43a-c** and from the amino group to the electron-withdrawing substituent in for **42d,e** and **43d,e** where the quinazoline fragment acts as a  $\pi$ -conjugated linker).

### Structures 42, 43

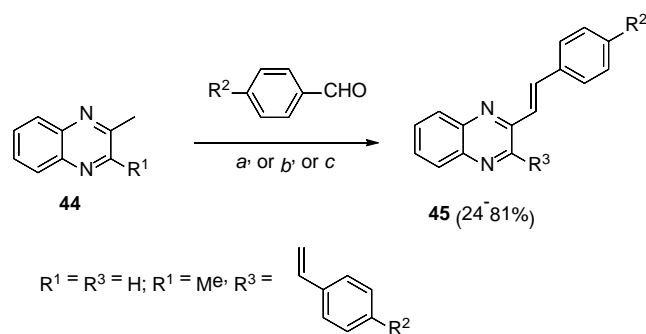


R = NMe<sub>2</sub> (**a**), OMe (**b**), H (**c**), R = CN (**d**), NO<sub>2</sub> (**e**); n = 1 (**42**), 2 (**43**)

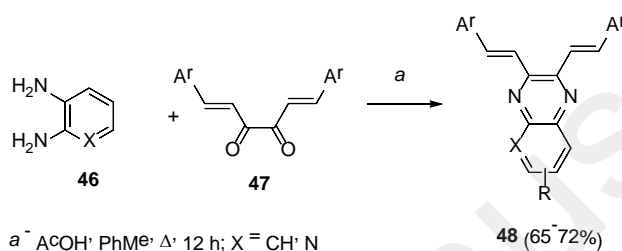
### II.1.3. Arylvinylquinoxalines

Various methods can be used to obtain 2-arylvinyl- and 2,6-diarylvinylquinoxaline derivatives, all leading exclusively to the *E*-isomers. The first one consists in Knoevenagel condensation between commercially available 2-methyl or 2,4-dimethylquinoxaline **44** and the corresponding arylcarboxaldehyde (Scheme 8, top reaction). Various conditions have been described; aqueous sodium hydroxide with Aliquat 336 as phase transfer catalyst,<sup>59</sup> NaH<sup>60</sup> or *t*BuOK<sup>61</sup> in THF. Another strategy consists in the condensation of a butanedione **47** bearing two arylvinyl substituents with an *o*-phenylenediamine derivative **46** (Scheme 8, bottom reaction).<sup>62</sup> Recently arylvinylquinoxalines **52** have been obtained by palladium-catalyzed C-H alkenylation of quinoxaline *N*-oxide intermediates **50** and subsequent reduction of derivatives **51**.<sup>63,64</sup> Compound **52** was synthesized from *N*-oxide **50** by iodine-catalyzed direct alkenylation of ethanedione **47** with styrol (Scheme 9). Direct arylalkenylation of furazan[3,4-*b*]pyrazines was presented as new approach to CH-functionalization.<sup>65</sup> Synthesis of 6-styryl-substituted 1,6-dihydropyrazine derivatives by reaction of 6-hydroxy adducts with styrylboronic acid was presented.<sup>66</sup>

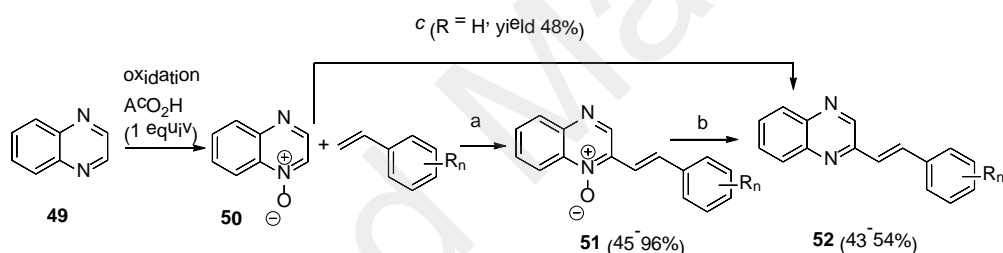
### Scheme 8



*a* - Aliquat 336 (Cat), 5 M NaOH,  $\Delta$ , 15 h;  $R = Cl, Br, SM, NMe_2, NPh_2, Cyclo(CH_2)_5$  (yields 24-78%);  
*b* - NaH, THF,  $N_2$ , rt, 2 h ( $R = NMe_2$  (83%),  $NPh_2$  (78%));  
*c* - Bu<sup>t</sup>OK, THF,  $\Delta$ , 16 h ( $R = N(CH_2CH_2)_2$  (84%))



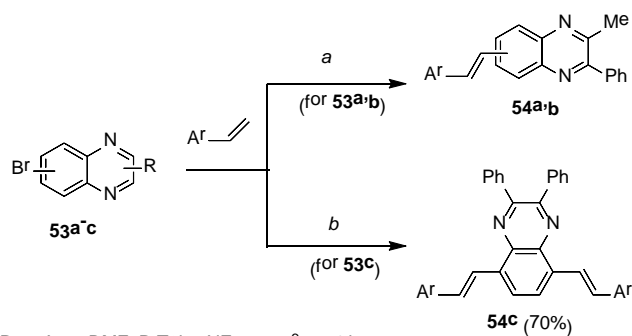
Scheme 9



*a* -  $Pd(OAc)_2$  (10 mol%), FmocVal-OH, 1:4 dioxane, AgOAc,  $N_2$ , 120 °C, 12 h; *b* - Zn,  $NH_4Cl$ , THF, rt, 40 min;  
*c* - C-H activation,  $I_2$  (2 mol%), air, DCM, 120 °C, 12 h;  $R_n = H, 4-CO_2Me, 4-OMe, 4-Br, 3,4-(OMe)_2$

6-Bromo-, 7-bromo- and 5,8-dibromoquinoline derivatives **53a-c** can be involved in Heck cross coupling reaction to yield the corresponding arylvinylquinolines **54a-c** (Scheme 10).<sup>67,68</sup>

Scheme 10

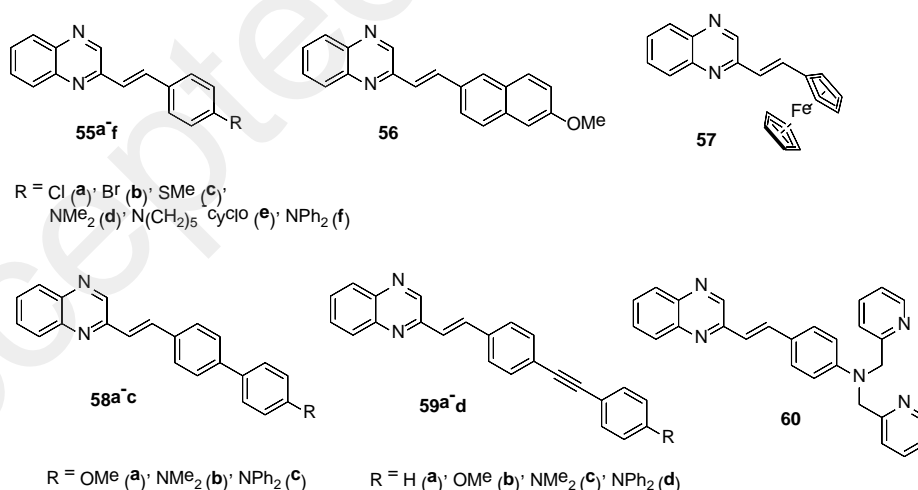


*a* -  $Pd(OAc)_2$ , DMF,  $P(Tol)_3$ ,  $NEt_3$ , 100 °C, 24 h;  
 $Ar = C_6H_4(NMe_2)_2$ ; *b* -  $Pd(OAc)_2$ , Bu<sub>4</sub>NBr, K<sub>2</sub>CO<sub>3</sub>, DMF, 90 °C, 48 h;  
 $Ar = C_6H_4N(C_6H_4)(OC_6H_4)_2$ ;  
**53**:  $R^1 = Me, R^2 = Ph$ ; isomers: 6-Br (**a**), 7-Br (**b**);  
 $R^1 = R^2 = Ph$ ; 5,8-Br<sub>2</sub> (**c**);  
**54**: 6-isomer (**a**, yield 48%), 7-isomer (**b**, 46%)



Achelle and coworkers have described a series of 2-arylvinyl quinoxalines **55-59**.<sup>59,69,70</sup> Compounds **58a-c** and **59a-d** have been obtained respectively by Suzuki and Sonogashira cross coupling reaction from compound **55b**. Amino derivatives **55d-f** exhibit yellow emission with high fluorescence quantum yield ( $\Phi_F = 0.59-0.70$ ) in DCM with strong positive emission solvatochromism in aprotic solvent of increasing polarity. Upon addition of trifluoroacetic acid, on solution of **55d,e**, a dramatic hypsochromic shift of the emission band is observed due to the protonation of the amino electron-donating group. In the case of compounds **56**, **58a** and **59b**, on the other hand, a progressive emission quenching attributed to the protonation of the quinoxaline fragment is observed. Biphenylenevinylene derivatives **58b,c** exhibit orange luminescence in DCM with lower fluorescence quantum yield ( $\Phi_F = 0.14-0.35$ ) but extended emission solvatochromic range with regards to their phenylenevinylene analogues **55d,e**. Compound **58a** exhibits blue luminescence with high fluorescence quantum yield ( $\Phi_F = 0.42$ ). In compounds **59b-d** the addition of a triple bond between the two phenylene linker lead to a red shift of absorption and emission with regards to their analogues **58a,b**, and red emission was observed for **59c** ( $\lambda_{em} = 647$  nm,  $\Phi_F = 0.07$ ). The second order NLO response of compounds **55b** and **59c,d** have been measured by the electric field induced second harmonic generation method (EFISH) and moderate  $\mu\beta$  values (respectively 300, 280 and  $200 \cdot 10^{-48}$  esu) have been measured in  $\text{CHCl}_3$ . The NLO response of compound **55d** has been also calculated theoretically by means of quantum chemical first principles calculations and calculated NLO response reproduce well the experimental value.<sup>71</sup>

### Structures 55-60



When comparing the photophysical properties of quinolin-2-yl, quinoxalin-2-yl, quinoxalin-4-yl and quinazolin-2-yl derivatives **29a**, **38a**, **40a** and **55d**, all bearing *N,N*-dimethylaminostyryl fragments (Table 1), it appears that the quinazoline derivative **55d** exhibits the most red-shifted emission and the highest fluorescence quantum yield in  $\text{CH}_2\text{Cl}_2$ .

**Table 1.** Photophysical properties of *N,N*-dimethylamino- and *N,N*-diphenylaminostyrylbenzo(di)azine derivatives in CH<sub>2</sub>Cl<sub>2</sub>

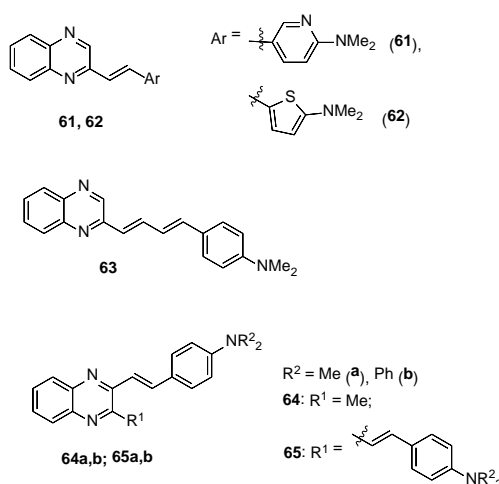
Compound	$\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/\text{mM}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{F}}$	References
<b>29a</b>	392 (27.0)	512	0.12	31
<b>38a</b>	395 (26.6)	536	0.21	54
<b>40a</b>	433 (18.0)	548	0.07	54
<b>55d</b>	427 (22.4)	570	0.59	59
<b>55f</b>	421 (25.4)	565	0.67	59
<b>58c</b>	393 (36.4)	632	0.35	59
<b>59d</b>	403 (35.7)	630	0.37	68

On the other hand, comparing the photophysical properties of *N,N*-diphenylamino substituted quinoxaline derivatives, the extension of the conjugation by adding a second phenylene fragment in the  $\pi$ -conjugated fragment results in a significant blue-shift of absorption and red-shift in emission associated with a reduction of quantum yield. The incorporation of a triple bond between the two phenylene fragment (compounds **58c**, **59d**) does not significantly modify the photophysical properties.

The same group has designed dipicolylamine fluorophore **60**. This compound exhibits yellow emission in MeCN ( $\lambda_{\text{em}} = 593\text{ nm}$ ,  $\Phi_{\text{F}} = 0.15$ ).<sup>55</sup> As shown by the previous series of compounds positive emission solvatochromism is observed in aprotic solvent as well as pH sensibility with a dramatic red shift on absorption band and emission quenching. Moreover a significant blue shift of the emission has been observed in the presence of Zn<sup>2+</sup> (and to a lesser extend with Cd<sup>2+</sup>) due to complexation of the dipicolylamine fragment reducing its electron-donating character and consequently the ICT into the chromophore.

Zhu and coworkers have designed 2-arylvinylquinazolines **61**, **62** and arylbutadienequinoxaline **64**.<sup>72</sup> In EtOH, **61** exhibits green luminescence with moderate fluorescence quantum yield ( $\lambda_{\text{em}} = 568\text{ nm}$ ,  $\Phi_{\text{F}} = 0.22$ ). In the same solvent, the emission quantum yield is much lower for **55d**, **62** and **63**. As far as **62** and **63** are compared, a significant red shift is observed for the butadiene derivative **63** ( $\lambda_{\text{em}} = 583\text{ nm}$ ). These compounds have been used for *in vivo* fluorescence detection of cerebral tau angles in Alzheimer's models.

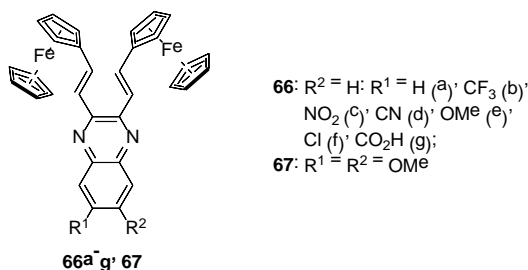
**Structures 61-65**



Zhao and coworkers have described aminostyrylquinoxaline chromophores **64**, **65** exhibiting yellow emission in DCM with a bathochromic shift of around 20 nm for disubstituted compounds **65** with regards to their monosubstituted analogues **64**.<sup>59</sup> As shown in other series of compounds, strong emission solvatochromism and pH sensitivity has been described. In addition, the chromophore **65b** exhibits reversible mechanofluorochromism: crystals exhibit yellow emission at 542 nm, red shifted to carmine emission at 592 nm upon grinding. Yellow emission can be recovered after fuming with DCM vapors.

Independently, Chauhan and coworkers<sup>73</sup> and Senthilkumar *et al*<sup>74</sup> have described a series of 2,3-di(ferrocenylstyryl)quinoxalines **66**, **67**. Compounds **66a,c,f,g** were exploited as photosensitizers in TiO<sub>2</sub>-based dye-sensitized solar cells and compounds **66c,g** revealed to be the most efficient with overall conversion efficiency of 3.38% and 4.42% respectively. The second order NLO properties of chromophores **66a-e** and **67** have been also studied by the EFISH method and negative  $\mu\beta$  values up to  $-960 \cdot 10^{-48}$  esu have been measured. Surprisingly high and stable second harmonic generation response in composite polymeric film has been also reported for **66b** ( $d_{33} = 5.27$  pm V<sup>-1</sup> in PMMA).

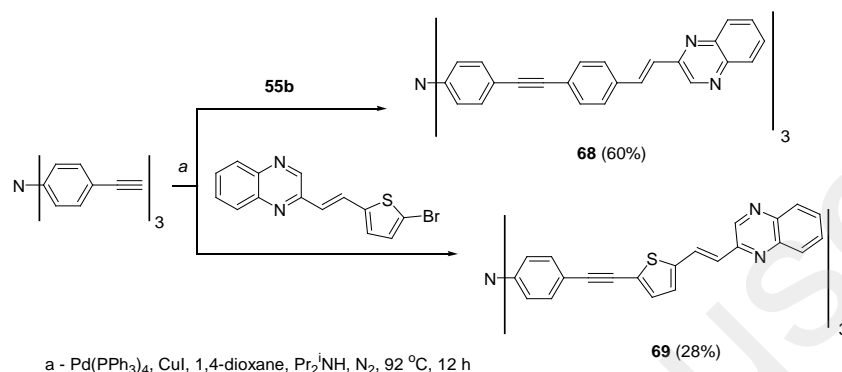
### Structures 66, 67



Cvejn and coworkers have designed the tripodal chromophores **68** and **69** with peripheral vinylquinazoline fragments (Scheme 11).<sup>75</sup> These compounds have been obtained with moderate yield by triple Sonogashira cross coupling reaction between tris(4-ethynylphenyl)amine and

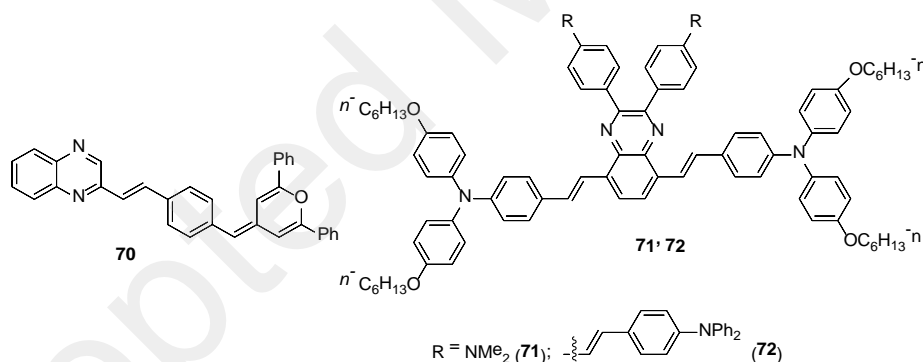
bromoarylvinylquinoxaline intermediates. Compounds **68**, **69** exhibit orange-red photoluminescence with high Stokes shifts ( $>6700\text{ cm}^{-1}$ ) in DCM (**68**:  $\lambda_{\text{em}} = 630\text{ nm}$ ,  $\Phi_{\text{F}} = 0.37$ , **69**:  $\lambda_{\text{em}} = 617\text{ nm}$ ,  $\Phi_{\text{F}} = 0.38$ ), strong emission solvatochromism and two-photon absorption properties with interesting two photon cross section (**68**:  $\sigma = 239\text{ GM}$  at  $780\text{ nm}$ , **69**:  $\sigma = 416\text{ GM}$  at  $760\text{ nm}$ ).

Scheme 11



Achelle and coworkers<sup>76</sup> have described the pyranilydene derivative **70**. This compound described as a potential 2<sup>nd</sup> order NLO chromophore, exhibits a significantly enhanced blue shifted emission upon protonation ( $\lambda_{\text{em}} = 479\text{ nm}$ ,  $\Phi_{\text{F}} = 0.25$ ).

Structures 70-72

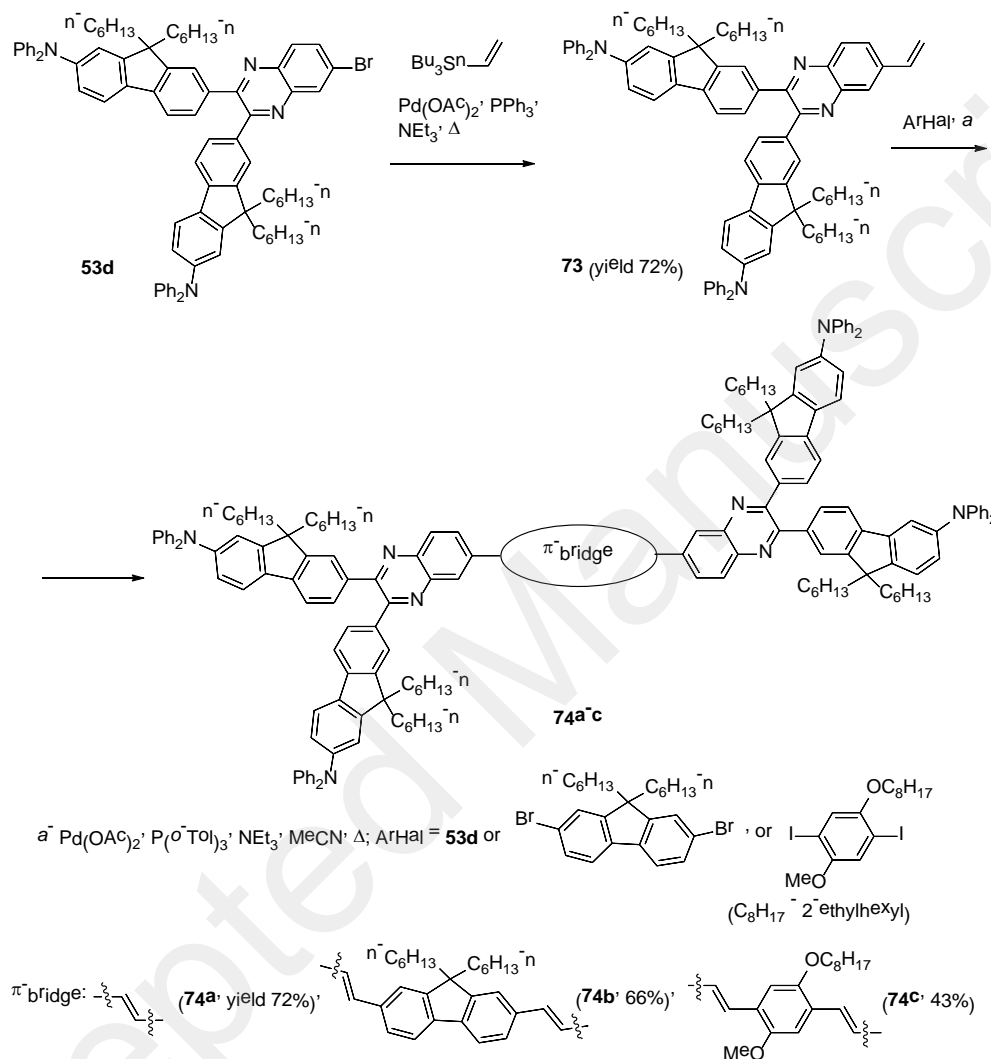


Chang and coworkers have designed multisubstituted quinoxaline chromophores **71** and **72**, chloroform solutions and thin films of these compounds exhibit yellow photoluminescence.<sup>68</sup> Photovoltaic cells (PVCs) and OLEDs were fabricated from **71** and by solution processing. While PVCs with a structure of  $\text{ITO}/\text{PEDOT:PSS}/\textbf{71}$  or  $\textbf{72}:\text{PC}_{71}\text{BM}/\text{Al}$  show the power conversion efficiencies of 0.31% and 0.45%, respectively, OLEDs with a structure of  $\text{ITO}/\text{PEDOT:PSS}/\textbf{71}$  or  $\textbf{72}/\text{LiF}/\text{Al}$  exhibit a maximum luminance (efficiency) of  $7.42\text{ cd/m}^2$  ( $0.034\text{ cd/A}$ ) and  $48.84\text{ cd/m}^2$  ( $0.032\text{ cd/A}$ ) with a turn-on voltage of 3.6 and 2.4 V, respectively.

Lin and coworkers have described three other multibranched quinoxaline chromophores **74a-c**. 6-Bromoquinoxaline **53d** is capable to react with tributylvinyltin in conditions of Stille cross-coupling reaction leading to 6-vinylquinoline **73**, which was used in Heck cross-coupling with

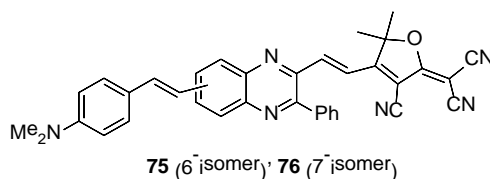
arylbromide for the synthesis of styrylderivatives **74a-c** (Scheme 12).<sup>77</sup> These compounds exhibit cyan luminescence in toluene as well as two-photon absorption with high cross section (**74a**:  $\sigma \sim 1250$  GM, **74b**:  $\sigma \sim 1680$  GM, **74c**:  $\sigma \sim 2300$  GM). Optical power limiting properties of compound **74b** have been also demonstrated.

Scheme 12



Kalinin and coworkers have proposed two push-pull chromophores **75** and **76** in which the quinoxaline linker plays the role of  $\pi$ -conjugated linker.<sup>67</sup> Red shifted absorption is observed for the isomer **76** ( $\lambda_{\text{abs}} = 600$  nm). DFT calculation has shown that this chromophore can be considered as a promising candidate for the development of 2<sup>nd</sup> order NLO materials.

Structures 75, 76



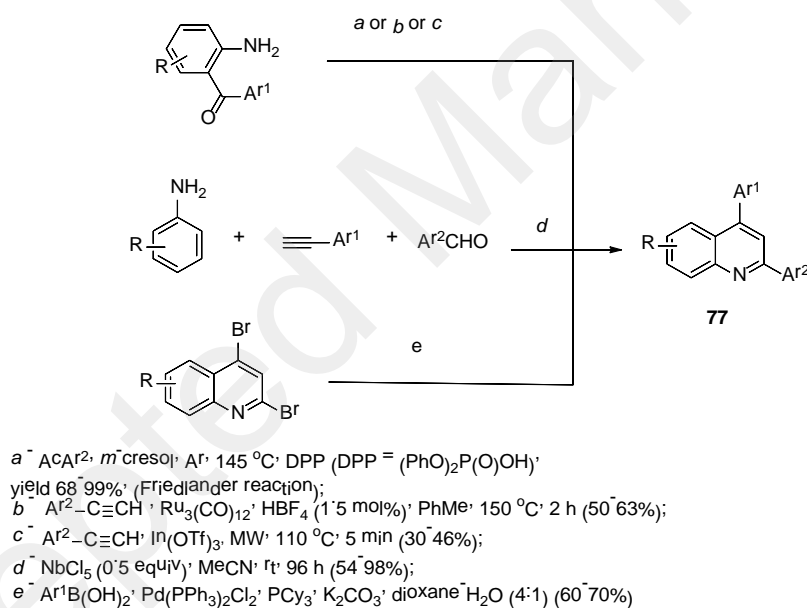
As shown with these examples, arylvinylbenzo(di)azine derivatives have been extensively studied for their luminescence, NLO and photovoltaic properties.

## II.2. Synthesis and photoluminescence of arylethynyl- and aryl(hetaryl)benzazines

### II.2.1. (Het)arylquinolines

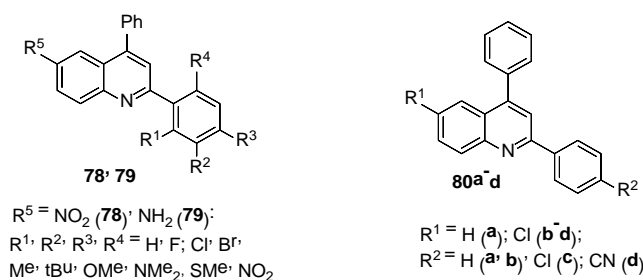
2,4-Diarylquinoline chromophores **77** are generally obtained by condensation reaction leading to the construction of the quinoline core. Various methods have been proposed including Friedländer condensation,<sup>78</sup> condensation of arylalkynes and *o*-aminobenzophenone derivatives,<sup>79</sup> or multicomponent reaction between arylaldehyde, anilines and arylalkynes (Scheme 13).<sup>80</sup> The Suzuki cross coupling reaction has been commonly used to afford 2-aryl-, 2,4-diaryl- or 4,6,8-triarylquinolines from 2-bromo, 2,4-dibromo and 6,8-dibromo-4-chloroquinoline derivatives respectively.<sup>32,78,81</sup> quinoline boronic ester have been also involved in Suzuki cross coupling to obtain 5/6-arylquinoline chromophores.<sup>82</sup>

Scheme 13



Carvalho dos Santos *et al* have described a series of 6-nitro- and 6-aminoquinolines **78** and **79**.<sup>83</sup> In EtOH, nitro derivatives **78** exhibit purple emission with low fluorescence quantum yield ( $\Phi_F < 0.03$ ) whereas amino analogues **79** exhibit blue emission with much stronger quantum yield ( $\Phi_F = 0.14$ – $0.83$ ). As expected, nitro substituents on the C2 phenyl ring of 6-aminoquinolines significantly reduce emission quantum yield.

Structures 78-80

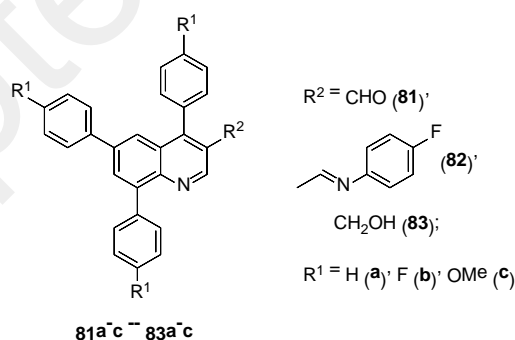


Kumar *et al* have studied the solid state (powder) emission of 2,4-diphenylquinoline **80a-c**.<sup>84</sup> For **80a,b** emission peak appears at 492 nm together with a weak shoulder at 536 nm, in case of **80c**, emission maximum is observed at 478 nm with a shoulder at 536 nm. For compounds **80a,b** the emission spectra are significantly broad due to  $\pi$ - $\pi^*$  interaction and/or conformational rigidity in the solid state, leading to chromacity coordinates not far from white light (0.28, 0.35).

Ghate and coworkers have synthesized cyano substituted quinoline derivative **80d**.<sup>85</sup> This compound exhibits purple luminescence ( $\lambda_{\text{em}} = 374\text{--}376$  nm with a shoulder at 395 nm) in various solvent (THF, DCM,  $\text{CHCl}_3$ ) with high emission quantum yield ( $\Phi_{\text{F}} = 0.69\text{--}0.75$ ) and blue emission ( $\lambda_{\text{em}} = 434$  nm) in solid state (powder).

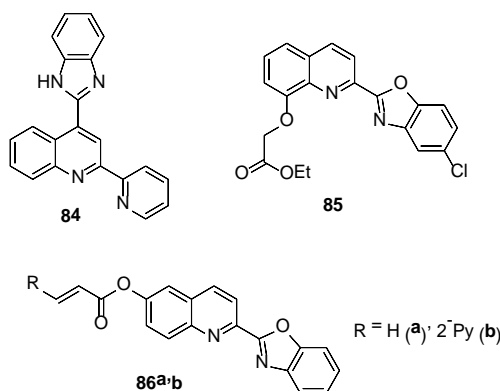
Mphahlele *et al* have described a series of 4,6,8-triarylquinoline derivatives **81-83**. These compounds exhibit purple-blue luminescence in  $\text{CHCl}_3$ .<sup>32</sup> Imines **82a-c** and methanol derivatives **83a-c** exhibit reduced emission intensity compared to the carbaldehyde analogues **81a-c**. The presence of methoxy substituents in compounds **81** and **83** leads to a significantly red-shifted emission (**81c**:  $\lambda_{\text{em}} = 470$  nm and **83c**:  $\lambda_{\text{em}} = 461$  nm).

### Structures 81-83



More *et al* and Han and coworkers have described the quinoline chromophores **84** and **85** respectively as  $\text{Cu}^{2+}$  fluorescent sensors.<sup>86,87</sup> Both compounds exhibit blue photoluminescence in solution (**84** in MeCN/HEPES buffer, **85** in the mixture EtOH- $\text{H}_2\text{O}$ ). The presence of  $\text{Cu}^{2+}$  ion caused selectively a great fluorescence quenching of this compound (ON-OFF probe) whereas, the addition of  $\text{Cd}^{2+}$  caused a weak reduction of emission intensity with a red-shift ( $\lambda_{\text{em}} = 380$  nm).

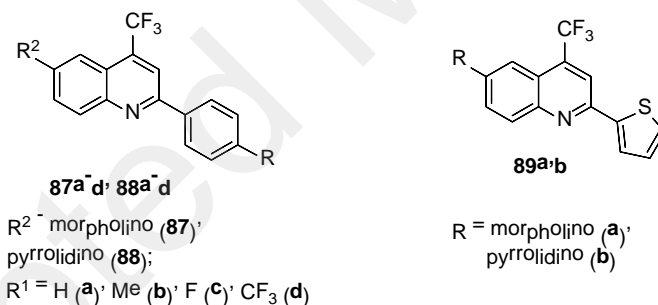
### Structures 84-86



Wu and coworkers have designed chromophores **86a,b** as selective probe for cysteine for bioimaging in living cell.<sup>88</sup> These probes can discriminate cysteine over other biothiol. Compound **86a** exhibits emission at 383 nm and quantum yield of 0.41 in EtOH/PBS 1:3. A ratiometric fluorescence response of **86a** toward cysteine with big peak-shifting to 518 nm is observed leading to detection limit below 1  $\mu\text{M}$ . Compound **86b** acts as an OFF-ON probe for cysteine.

Bonacorso and coworkers have designed a series of amine-substituted 2-aryl-4-trifluoromethylquinolines **87-89**.<sup>89</sup> These compounds that show blue luminescence ( $\lambda_{\text{em}} = 468\text{--}482$  nm) with moderate emission quantum yield ( $\Phi_{\text{F}} = 0.05\text{--}0.18$ ) in chloroform, exhibit strong interaction with ct-DNA and can be used for DNA titration.

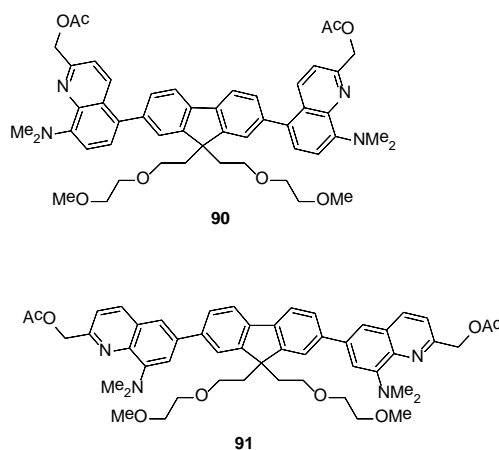
#### Structures 87-89



Tran *et al* have described 8-dimethylaminoquinoline-derived quadrupolar two-photon absorption chromophores **90** and **91**.<sup>82</sup> These compounds that exhibit low luminescence ( $\Phi_{\text{F}} = 0.04\text{--}0.12$ ) and moderate two-photon cross section (**90**:  $\sigma = 25$  GM at 680 nm and **91**:  $\sigma = 10$  GM at 700 nm), have been designed for two-photon acetyl uncaging application.

#### Structures 90, 91



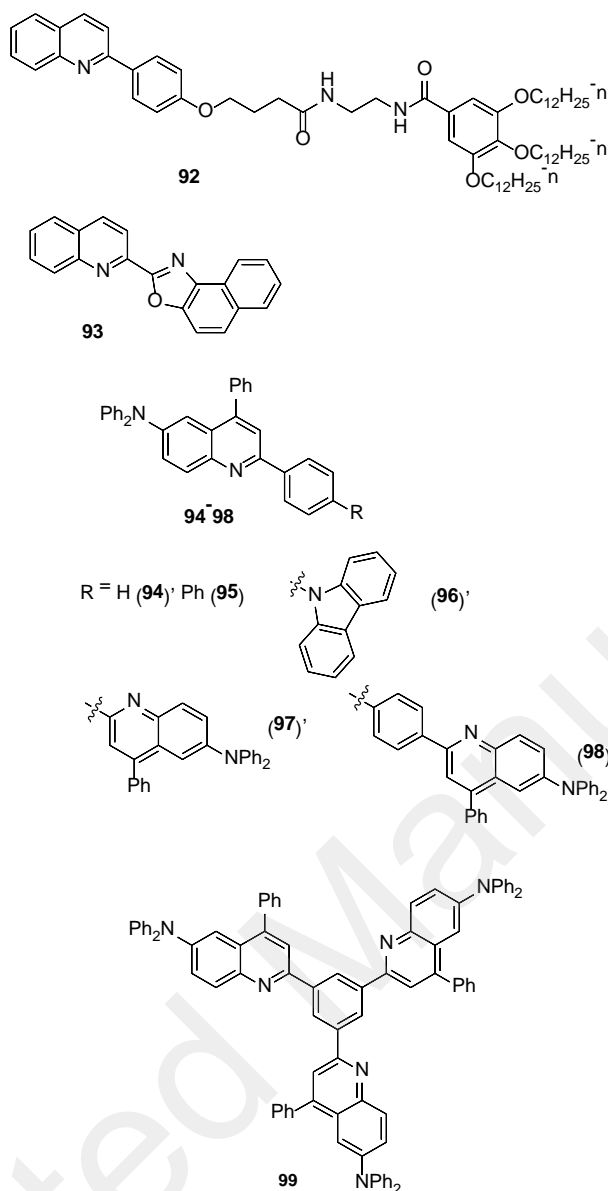


Cao and coworkers have designed chromophore **92**.<sup>81</sup> This compound forms organogel in various solvents. When self-assembled into organogel in MeCN, **92** exhibits two emission peaks at 385 nm and 495 nm due to  $\pi$ - $\pi$  stacking interactions in the gel state are observed. Solution and organogel of **92** in MeCN selectively and reversibly respond to volatile acid and organic amine vapors.

In addition to compound **31**, Zanocco *et al* have described an analogue **93** without vinyl linker.<sup>49</sup> As expected, **93** exhibits blue shifted emission with regards to **31** (410 nm for **93** and 450 nm for **31**) but the quantum yield remains close to 1 in benzene. As for **31**, compound **93** exhibits intense white light emission in MeOH (for 15% of DMSO, the chromacity coordinates are 0.28, 0.35) with higher emission quantum yield than **31** (0.42 vs 0.31).

Lee and coworkers have designed diphenylamino substituted quinoline chromophores **94-99**.<sup>78</sup> These compounds exhibit blue photoluminescence in toluene with high quantum yield (>90%) attributed to charge transfer from the diphenylamino group to the quinoline ring. OLEDs have been fabricated with these chromophores with external quantum efficiency in the range of 1.2–2.3%.

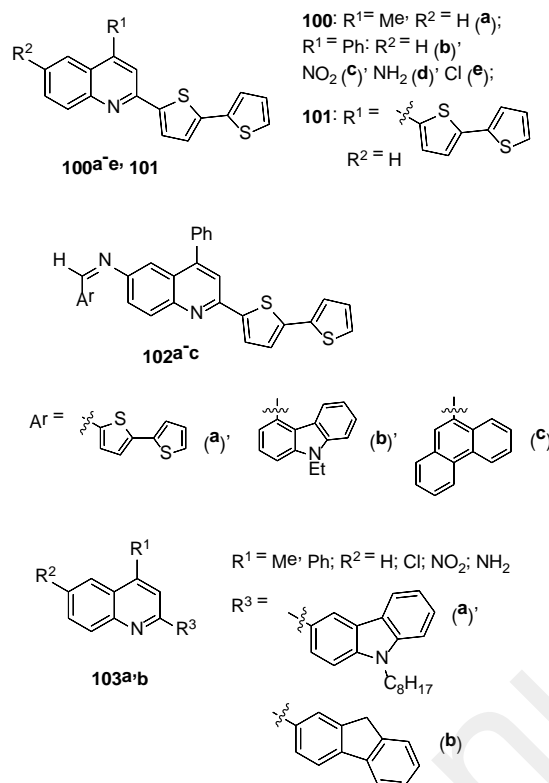
#### Structures 92-99



Slodek and coworkers<sup>79</sup> have designed quinoline chromophores with a 2,2'-bithiophene fragment **100a-e**, **101**. Compounds **100** and **101** exhibit blue-green emission in DCM ( $\lambda_{em} = 444\text{--}479\text{ nm}$ ) with moderate Stokes shifts and microsecond lifetime whereas orange-red fluorescence is observed for **100c** ( $\lambda_{em} = 595\text{ nm}$ ) with a larger Stokes shift ( $7465\text{ cm}^{-1}$ ). Starting from **100d**, the same team has described a series of Schiff bases **102a-c**.<sup>90</sup> The compounds **102** exhibit moderately strong blue emission in solution as well as in PMMA blend whereas green emission is observed in polyvinylcarbazole matrix. When mixed with silver nanowires, these compounds exhibit strong electroluminescence due to plasmonic enhancement.

The same team<sup>91</sup> has also compared bithiophene quinoline chromophores **100** with their carbazyl analogues **103a**. Stronger ICT occurs in carbazyl substituted quinoline **103a** with regards to **100**, and the carbazyl substituent leads to higher quantum yield and lifetime (respectively up to 0.7 and 5.72 ns for **103a**). Applications as fluorescent cellular probes have been proposed.

### Structures 100-103

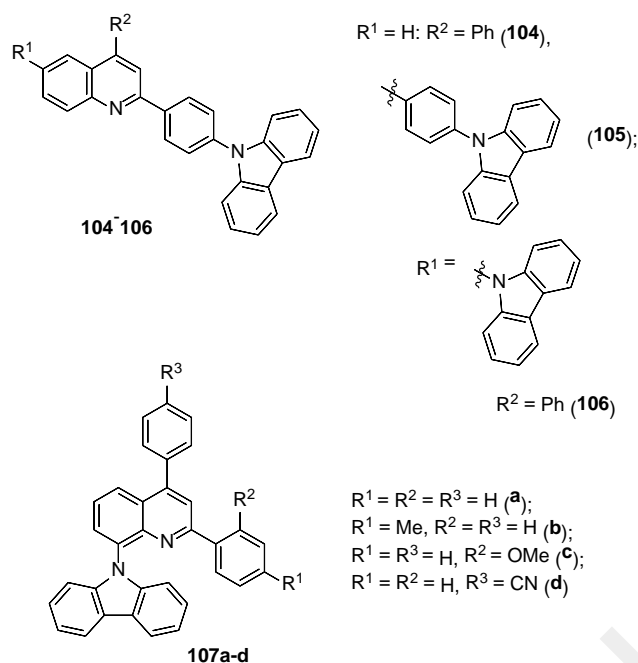


In the later work<sup>92</sup> the same group described the series of quinolines **103b**, bearing fluorenyl fragment at the position 2. These compounds exhibit emission with  $\lambda_{\text{em}}$  in the range of 400–560 nm, the presence of nitro group leads to the red shift; the luminescence quantum yield from 0.6 to 0.30. Fluorenyl derivative **103b** possesses glass-forming properties; the obtained films as well as solid samples exhibit fluorescence. The cyclic voltammetry showed that these compounds undergo multistep oxidation and reduction. Their semiconductor properties were studied, the derivative **103b** (R<sup>1</sup> = Me, R<sup>2</sup> = H) was tested as a component of the active layer for the solar cell.

Chen *et al* have designed carbazole-quinoline hybrids **104–106** as host for orange and deep-red phosphorescent OLEDs.<sup>93</sup> The optimized orange phosphorescent OLEDs using **104** exhibit an external quantum efficiency of 25.6% and a power efficiency of 68.1 lm/W.

Bhattacharjee *et al* have designed carbazole-quinoline conjugates **107a–d** exhibiting dual emission resulting from thermally activated delayed fluorescence and room temperature phosphorescence.<sup>94</sup> The authors stated that these compounds have great promise for high-efficiency white OLEDs.

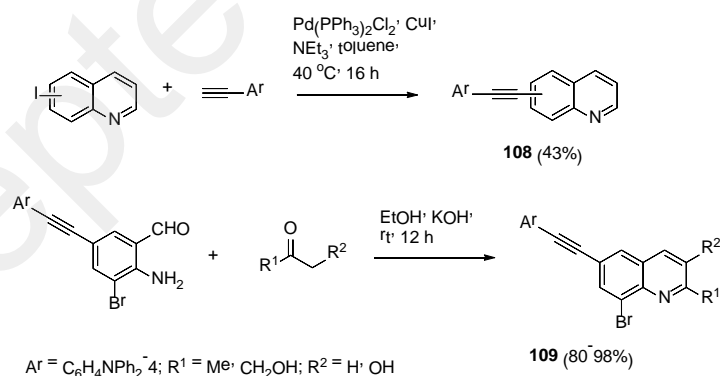
## Structures 104–107



## II.2.2. Arylethynylquinolines

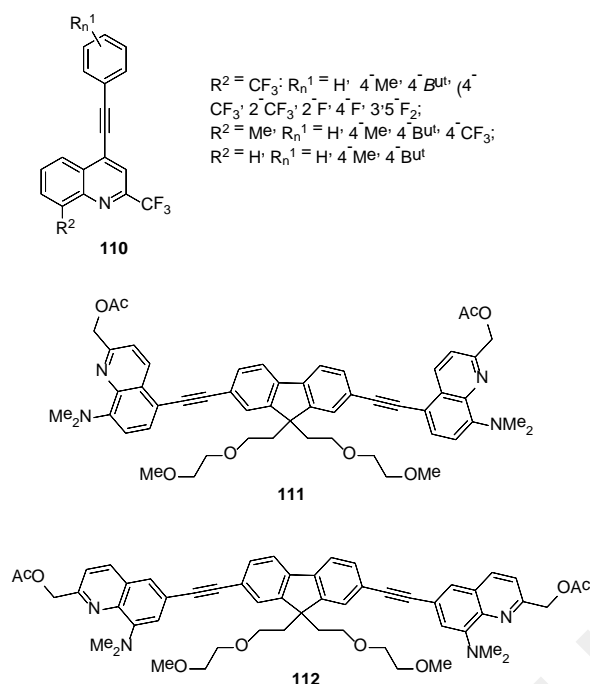
5-, 6- and 8-Arylethynylquinolines **108** can be easily obtained by Sonogashira cross coupling reaction from the corresponding iodoquinolines (Scheme 14, top reaction).<sup>82,95</sup> The same strategy can be used to obtain 4-arylethynylquinoline from the corresponding chloro intermediate.<sup>96</sup> 6-Arylethynylquinolines **109** have been also obtained by Friedländer condensation from arylethynyl substituted aminobenzaldehyde (Scheme 14, bottom reaction).<sup>97</sup>

**Scheme 14**



Alapour *et al* have designed a series of trifluoromethyl substituted 4-arylethynylquinolines chromophores **110**. These compounds exhibit blue luminescence in MeCN solution and in solid state.<sup>96</sup> In solid state, the addition of  $\text{CF}_3$  substituents was found to result in increased flexibility of the structure with a decrease in the number of intermolecular interactions and the authors stated that it could result in enhancement their emission in solid state.

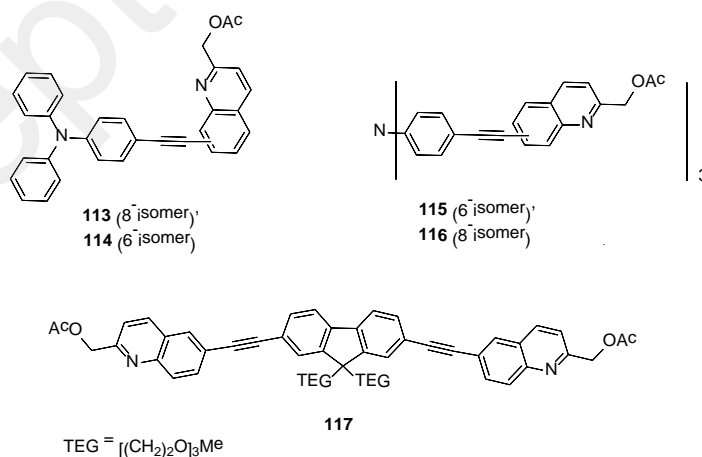
## Structures 110-112



In addition to arylquinolines **90** and **91**, Tran and coworkers<sup>82</sup> have designed their arylethynyl analogues **111** and **112** as two-photon absorption chromophores for acetyl uncaging. In comparison with their analogues **90**, **91**, compounds **111**, **112** exhibit enhanced two-photon cross section (**111**:  $\sigma = 160$  GM at 720 nm and **112**:  $\sigma = 70$  GM at 710 nm).

The same team has also developed the chromophores **113-117** for the same application.<sup>95</sup> These compounds exhibit blue emission in THF with high emission quantum yield ( $\Phi_F = 0.59-0.68$ ). Quadripolar compound **117** exhibit the lowest two-photon cross section ( $\sigma = 75$  GM at  $\lambda = 710$  nm) whereas the higher value is observed for **116** ( $\sigma = 480$  GM at  $\lambda = 730$  nm).

#### Structures 113-117

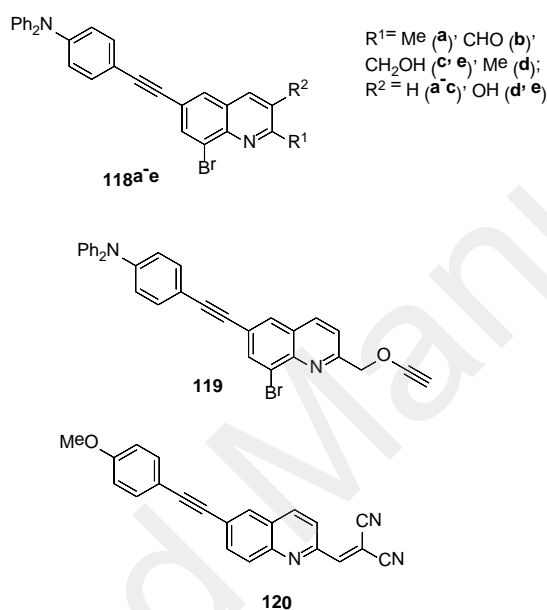


Picard and coworkers have designed a series of diphenylamino-substituted 6-arylethynyl,8-bromoquinolines **118**.<sup>97</sup> These chromophores combine in toluene significant two photon absorption cross section ( $\sigma = 116-265$  GM) in the NIR region, good photosensitization ability ( $\Phi_\Delta = 0.4-0.6$ ) and fluorescence properties ( $\Phi_F = 0.2-0.6$ ). The authors described these compounds as promising

dyes for combining two-photon imaging and photodynamic therapy. Compound **118c** has been used as precursor to obtain **119** that can be graphed on mesoporous silica nanoparticles via click chemistry for two-photon photodynamic therapy.<sup>98</sup>

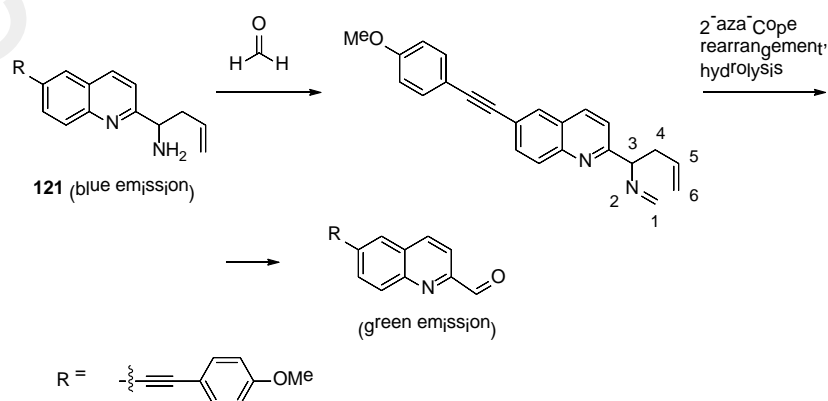
Ning and coworkers have designed chromophore **120** as two-photon viscosity probe.<sup>99</sup> It was shown that increasing the water/glycerol mixture viscosity, which blocking the rotation of the dicyanovinyl group, leads to strong enhancement of emission intensity of compound **120** upon two-photon excitation. The effectiveness of application of this compound as fluorescent probe depending on the environment viscosity was shown *in vivo* on cervical tumor cells HeLa.

Structures 118-120



Yang *et al* have designed a two-photon fluorescent probe **121** for selective detection of endogenous formaldehyde via Aza-Cope reaction (Scheme 15).<sup>100</sup> In PBS buffer, compound **121** shows an emission maxima at 405 nm ( $\Phi_F = 0.03$ ,  $\sigma = 185 \text{ GM}$ ), upon addition of formaldehyde, emission maxima is red shifted at 490 nm ( $\Phi_F = 0.10$ ,  $\sigma = 275 \text{ GM}$ ).

Scheme 15

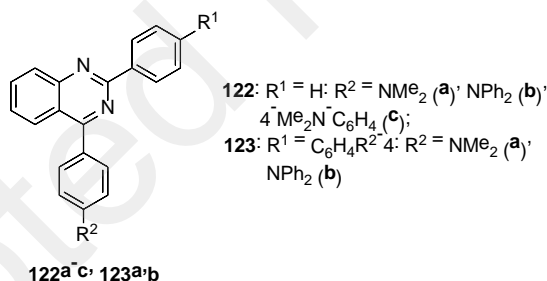


### II.2.3. (Het)arylquinazolines

Two main methods have been used to synthesize arylquinazoline derivatives. The 1<sup>st</sup> one consists in condensation reactions to build the quinazoline core and the second one in Suzuki cross coupling reaction from halogenoquinazolines. 2-Arylquinazolines can be obtained by reaction of 2-aminobenzamide with arylcarboxaldehyde.<sup>101</sup> 4-Arylquinazoline can be obtained by Suzuki cross coupling reaction from chlorine intermediates<sup>54</sup> or by iodine-catalyzed oxidative C-H amination from *ortho*-carbonyl-substituted anilines and ammonia.<sup>102</sup> 2,4-Diarylquinazolines can be obtained either by double Suzuki cross coupling (the C4 position being more reactive than the C2 one),<sup>54</sup> by condensation reaction from 2-cyanoaniline<sup>103</sup> or by condensation of 2-aminobenzophenone with arylcarboxaldehyde.<sup>104</sup> 6-Arylquinazoline can be also obtained from 6-bromo or 6-iodoquinazoline by Suzuki cross-coupling.<sup>57,101</sup>

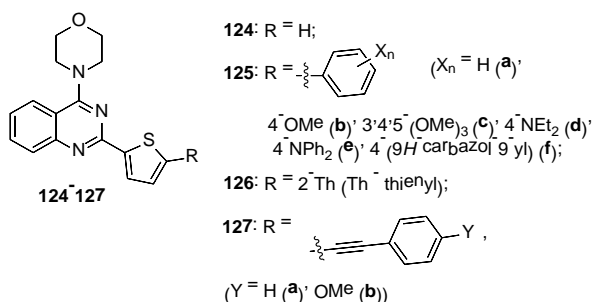
Achelle and coworkers have synthesized 4-aryl and 2,4-diarylquinazolines **122**, **123**.<sup>54,105</sup> In DCM, compound **122a** exhibits blue photoluminescence whereas compounds **122b** and **123a,b** exhibit green luminescence and **122c** emits yellow-orange light. 4-Arylquinazolines **123a,b** exhibit significantly higher quantum yield ( $\Phi_F = 0.8-0.93$ ) than their 2,4-diarylquinazoline **123** ( $\Phi_F = 0.30-0.34$ ) and 4-arylvinylquinazoline ( $\Phi_F = 0.02-0.25$ ) analogues. As expected with regards to their arylvinyl analogues **40** and **41**, compounds **122**, **123** show blue shifted emission.<sup>54</sup>

#### Structures 122, 123



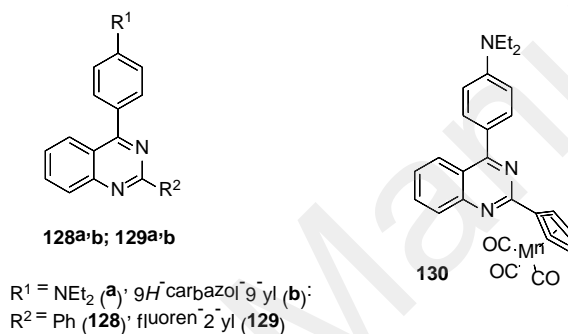
Nosova and coworkers have designed a series of 4-morpholin-4-yl substituted quinazoline **124-127**. These compounds have been obtained by bromination of **124** followed by palladium catalyzed Suzuki/Sonogashira cross coupling reaction.<sup>106</sup> Compounds **125d,e** exhibit green photoluminescence in MeCN whereas compounds **125b,c** and **126**, **127** show blue photoluminescence. pH sensibility with significant red-shifted emission has been demonstrated. Cyano analogue **125e** is poorly emissive ( $\lambda_{em} = 471$  nm,  $\Phi_F < 0.01$ ).<sup>107</sup>

#### Structures 124-127



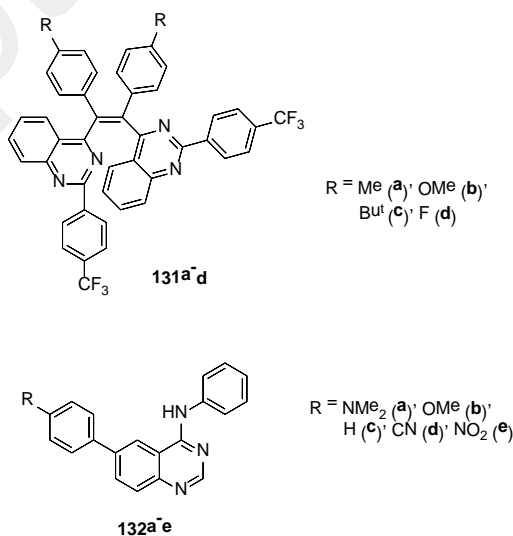
The same group has described a series of 2,4-diarylquinazoline derivatives **128-130**.<sup>108</sup> These compounds exhibit blue luminescence in toluene ( $\lambda_{em} = 431-459$  nm) with emission quantum yield up to 0.82 for **128a** whereas orange emission is observed for the same compounds in MeCN with lower quantum yield ( $\Phi_F = 0.05-0.28$ ).

### Structures 128-130



Wang and coworkers have designed a series of 2-arylquinazolines-substituted ethene derivatives including chromophores **131a-d**.<sup>109</sup> These compounds exhibit typical aggregation induced emission properties. As a typical example, compound **131b** exhibits green emission ( $\lambda_{em} = 530$  nm) in thin film with high quantum yield ( $\Phi_F = 0.52$ ).

### Structures 131, 132



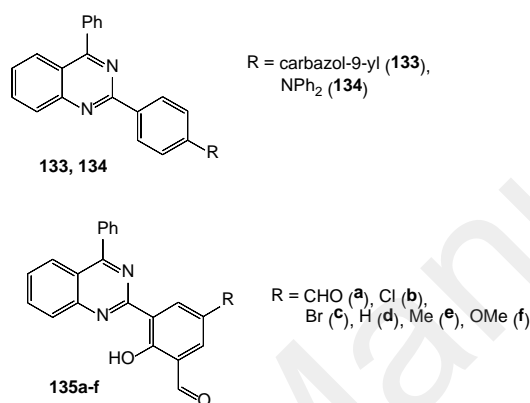
In addition to 6-arylvinylquinazoline derivatives **42** and their butadiene analogues **43**, Dhuguru et al<sup>57</sup> have designed 6-arylquinazoline chromophores **132a-e**. Except dimethylamino



derivative **132a** ( $\lambda_{\text{em}} = 435$  nm,  $\Phi_{\text{F}} = 0.37$  in  $\text{CHCl}_3$ ), these compounds are poorly emissive ( $\Phi_{\text{F}} < 0.03$ ) with blue shifted emission with regards to their vinyl or butadiene analogues **40-42**.

Liu and coworkers have designed chromophores **133** and **134**.<sup>103</sup> These compounds can be used for white photoluminescence and electroluminescence combining the blue emitting neutral form and orange-emitting protonated form. Indeed the protonation of the quinazoline ring greatly enhances its electron-withdrawing character and strengthens the ICT leading to bathochromically shifted emission.

### Structures 133-135

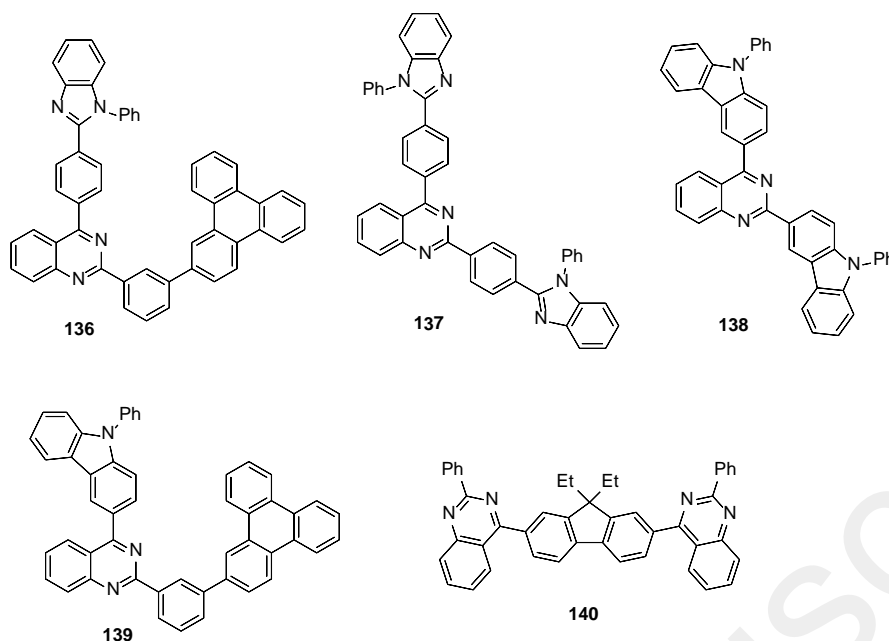


Dwivedi *et al* have designed a series of quinazoline-based excited state intramolecular proton transfer (ESIPT) active systems **135a-f**.<sup>104</sup> The ESIPT emission, completely quenched in solution, can be restored via aggregation-induced emission. In solid state, these compounds exhibit various emission band corresponding to the enol ( $\lambda_{\text{em}} = 465\text{--}513$  nm) and keto forms ( $\lambda_{\text{em}} = 560\text{--}704$  nm). The authors claim that these tunable ESIPT emissive materials have potential applications in optoelectronic devices.

Zhang and coworkers have described a series of 2,4-diarylquinazoline derivatives with benzoimidazole, carbazole and triphenylene substituents **136-139**.<sup>110</sup> These compounds can be used as host material for red phosphorescent organic light-emitting diodes. The best device was obtained with **136** with external quantum efficiency of 19.2%, current efficiency of 18.3 cd/A and 21.3 lm/W.

Kim and coworkers have designed fluorene-bridged quinazoline derivatives **140**. This compound exhibits in DCM solution and thin film.<sup>111</sup> A blue OLED with external quantum efficiency of 1.58% at 20 mA/cm<sup>2</sup> has been obtained with this compound.

### Structures 136-140



#### II.2.4. Arylethynylquinazolines

Arylethynylquinazoline chromophores have been synthesized exclusively by Sonogashira cross coupling reactions.<sup>54</sup> 4-Arylethynylquinazolines can be obtained from the corresponding chloro derivatives. 6-iodo/bromo- and 6-iodoquinazolines can lead to 6-arylethynyl and 8-arylethynylquinazolines.<sup>112,113</sup> To the best of our knowledge, no 2-ethynylarylquinazoline chromophores have been designed so far.

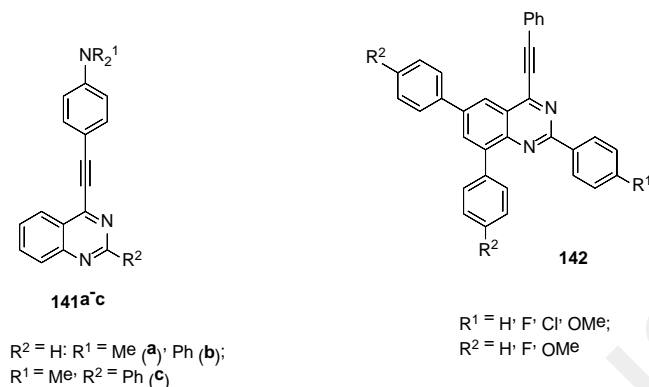
Achelle and coworkers have proposed 4-arylethynylquinazolines **141a-c**.<sup>54</sup> In DCM solution, these compounds exhibit green emission ( $\lambda_{em} = 551\text{--}565\text{ nm}$ ) with low quantum yield, except the diphenylamino derivative **141b** ( $\Phi_F = 0.41$ ). As shown in Table 2, 4-arylethynylquinazolines **141** and 4-arylvinylquinazolines **40** exhibit red-shifted emission and lower quantum yield than their 4-arylquinazoline analogues **122**.

**Table 2.** Comparison of photophysical properties of 4-arylethynylquinazolines **141**, 4-arylvinylquinazolines **40** and 4-arylquinazoline analogues **122** in  $\text{CH}_2\text{Cl}_2$ .<sup>54</sup>

Compound	$\lambda_{abs}/\text{nm}$ ( $\epsilon/\text{mM}^{-1}\text{ cm}^{-1}$ )	$\lambda_{em}/\text{nm}$	$\Phi_F$
<b>141a</b>	411 (27.5)	560	0.03
<b>40a</b>	433 (18.0)	548	0.07
<b>122a</b>	380 (16.4)	490	0.93
<b>141b</b>	414 (29.2)	565	0.41
<b>40b</b>	429 (16.9)	571	0.25
<b>122b</b>	384 (16.6)	528	0.80

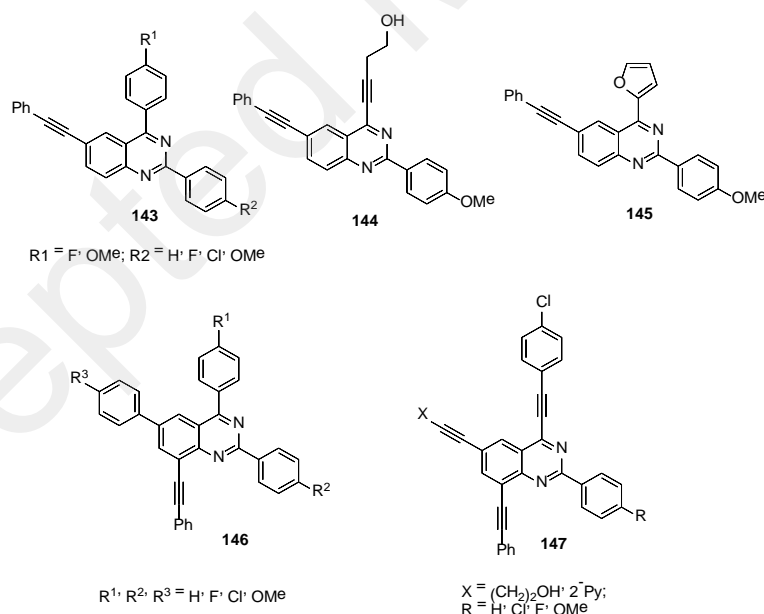
Mphahlele *et al* have designed a series of 2,6,8-triaryl-4-arylethynylquinazoline derivatives **142**.<sup>114</sup> In  $\text{CHCl}_3$ , these compounds exhibit blue luminescence ( $\lambda_{\text{em}} = 454\text{--}480\text{ nm}$ ) with low quantum yield ( $\Phi_{\text{F}} = 0.10\text{--}0.07$ ).

#### Structures 141, 142



Mphahlele and coworkers have designed a series of 6-phenylethynylquinazoline derivatives **143-145** and the same teams have also synthesized 8-phenylethynylquinazolines **146**, as well as 4,8-biarylethynyl- and 4,6,8-triarylethynylquinazolines **147**.<sup>112,113</sup> These compounds exhibit also blue emission in  $\text{CHCl}_3$  with low to moderate quantum yield.

#### Structures 143-147

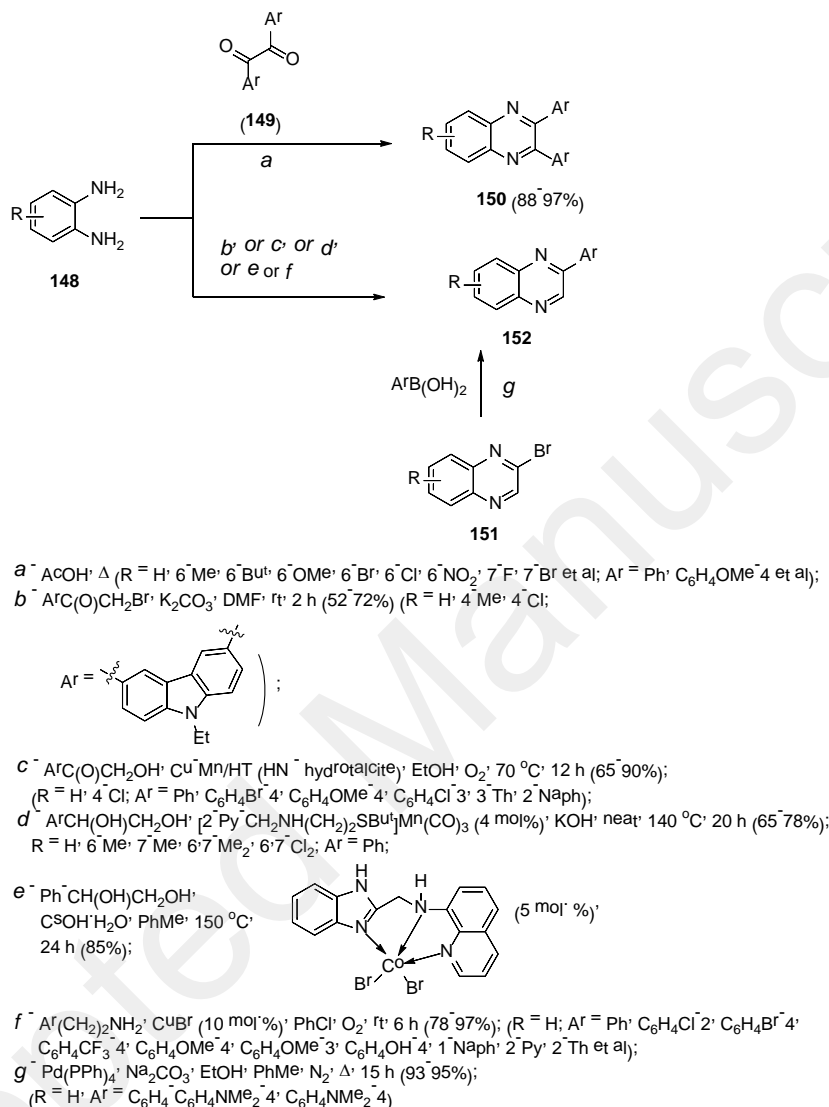


### II.2.5. (Het)arylquinoxalines

2,4-Diarylquinoxalines **150** are generally obtained by condensation of *o*-phenylenediamine **148** and diaryl 1,2-diketone derivatives **149** (Scheme 16,a).<sup>115-117</sup> 2-Arylquinoxalines **152** can be obtained by condensation reaction between *o*-phenylenediamine **148** and  $\alpha$ -bromo-arylketone

(b),<sup>117,118</sup>  $\alpha$ -hydroxy-arylketone (c),<sup>119,120</sup> phenylethane-1,2-diol (d or e)<sup>121,122</sup> or 2-arylethylamines (f).<sup>123</sup> Another strategies consist in Suzuki cross-coupling reaction from 2-chloroquinoxaline **151**,<sup>105</sup> as well as nucleophilic substitution of hydrogen in quinoxalin-N-oxides.<sup>124</sup>

Scheme 16



5-Aryl-, 6-aryl- and 5,8-diarylquinoxalines can be easily obtained by Suzuki or Stille cross coupling reactions from the corresponding bromo or iodo derivatives.<sup>111,125,126</sup>

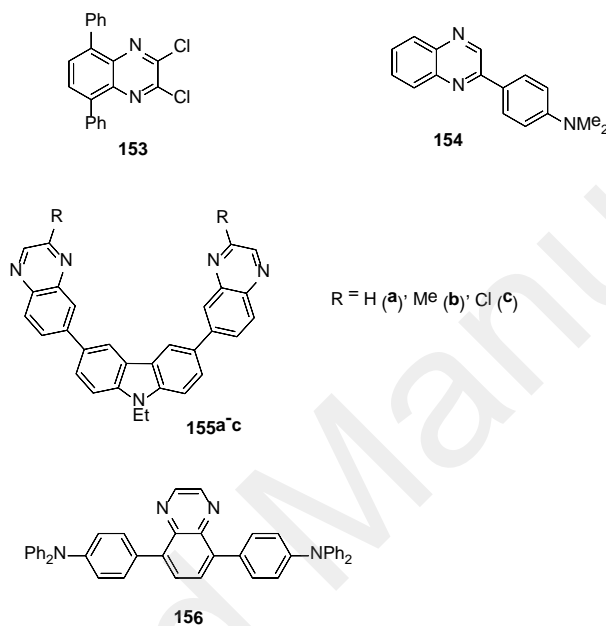
Nafe and coworkers have synthesized chromophore **153** that exhibits blue luminescence in solution (unspecified solvent,  $\lambda_{\text{em}} = 467$  nm,  $\Phi_{\text{F}} = 0.6$ ).<sup>127</sup>

Achelle *et al.* have synthesized chromophore **154**.<sup>105</sup> This compound exhibits green-yellow luminescence ( $\lambda_{\text{em}} = 539$  nm) with high fluorescence quantum yield ( $\Phi_{\text{F}} = 0.90$ ) in DCM. Design of experiment methodology combined with ANOVA method have shown that compared with diazine fragment the benzodiazine part led to a significant red shift in absorption and emission.

Telore and coworkers have synthesized carbazole derivatives **155a-c**.<sup>118</sup> These compounds exhibit blue luminescence in DCM and emission solvatochromism attributed to ICT and are therefore potential NLO chromophores.

Lu and coworkers have designed D-A-D chromophore **156**.<sup>128</sup> This compound exhibits yellow-green emission ( $\lambda_{em} = 557$  nm) in DCM due to ICT from diphenylamino groups to the central quinoxaline core. Bulk heterojunction solar cell application has been also proposed for this compound.<sup>129</sup>

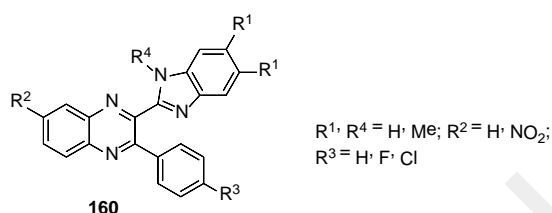
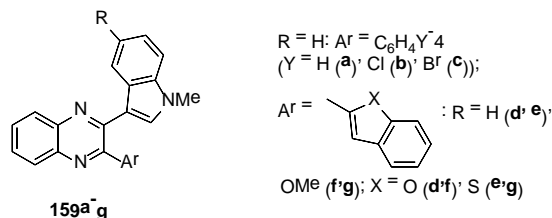
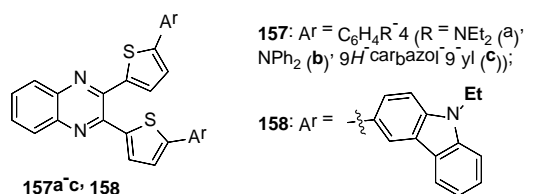
#### Structures 153-156



Moshkina and coworkers have described a series of V-shaped 2,3-bis(5-arylthiophen-2-yl)quinoxaline derivatives **157a-c**, **158**.<sup>115</sup> These compounds exhibit blue-green emission ( $\lambda_{em} = 498$ – $557$  nm) in toluene with moderate quantum yield ( $\Phi_F = 0.14$ – $0.07$ ). The highest quantum yield is observed for the diphenylamino derivative **157b**. These compounds exhibit halochromism and the ability of **157a** to function as colorimetric and luminescent pH sensor has been demonstrated. The addition of TFA (up to 135 equiv) led to a blue shifted emission (from 547 nm to 461 nm) attributed to the protonation of the diethylaminophenyl moieties.

Zhang and coworkers have designed chromophores **159a-g**.<sup>130</sup> These compounds exhibit blue-green luminescence in DCM (494–530 nm) as well as emission solvatochromism.

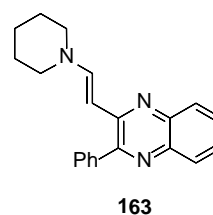
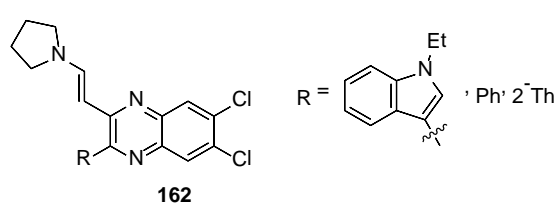
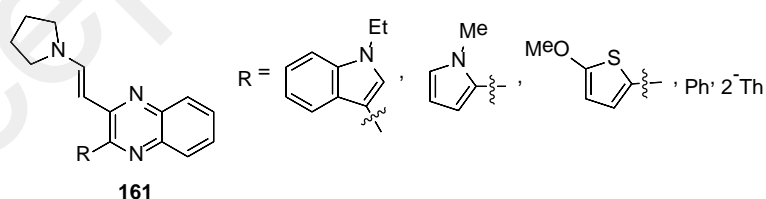
#### Structures 157-160



Burdanov *et al* designed benzimidazolylquinoxalines **160** as novel fluorophores with tunable sensitivity to solvent effects.<sup>131</sup> The wavelengths of lowest-energy absorptions in the spectra of various solutions of **160** vary in the range 352–396 nm, whereas the wavelengths of emission maxima vary in the rather broad range 440–519 nm ( $\Phi_F$  0.03–0.29). It was found that the addition of small amounts of DMF or DMSO in the solution of **160** (R<sup>2</sup> = NO<sub>2</sub>, R<sup>3</sup> = Cl, R<sup>4</sup> = R<sup>1</sup> = H) in DCM results in a dramatic quenching of the fluorescence.

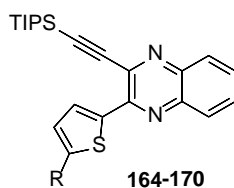
Gers-Panters and coworkers have designed a series of 2-aryl-3-aminovinylquinoxalines **161**–**163**. These compounds exhibit intense yellow emission in DCM ( $\Phi_F$  up to 0.61) with pronounced emission solvatochromism and photochromic fluorescence quenching.<sup>132</sup>

### Structures 161-163

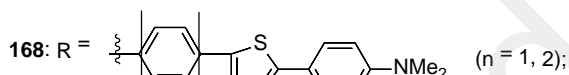
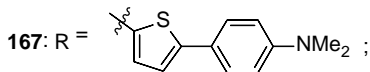
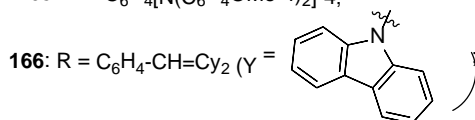


Merkt *et al.* have described a series of 2-thiophenyl-2-yl-*t*-ethynylquinoxalines **164-176**. These compounds exhibit blue to yellow emission in DCM depending of the substituent with emission quantum yield up to 0.75 for **164a** and **164j**.<sup>133,134</sup> Aggregation induced emission phenomena has been demonstrated for compounds **165** and **169**: whereas methanol solution of these compounds are non emissive, the addition of water leads to yellow/pink emission. Compounds **165** and **170** are also emissive in solid state (powder and doped thin film of PMMA).

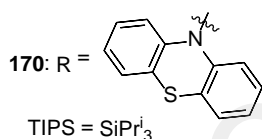
### Structures 164-176



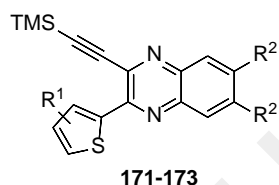
**164:** R = C<sub>6</sub>H<sub>4</sub>X<sub>n</sub> (X<sub>n</sub> = H (**a**), 4-NMe<sub>2</sub> (**b**), 4-OMe (**c**), 4-Me (**d**), 4-CH<sub>2</sub>OH (**e**), 4-Cl (**f**), 4-CN (**g**), 4-NO<sub>2</sub> (**h**), 4-CHO (**i**), 2,6-(OMe)<sub>2</sub> (**j**);  
**165:** R = C<sub>6</sub>H<sub>4</sub>[N(C<sub>6</sub>H<sub>4</sub>OMe-4)<sub>2</sub>]-4;



**169:** R = NPh<sub>2</sub>;



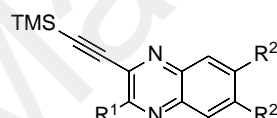
TIPS = SiPr<sub>3</sub>



**171:** R<sup>2</sup> = H, R<sup>1</sup> = H, Me, Bu<sup>t</sup>, SMe, OMe, NMe<sub>2</sub>;

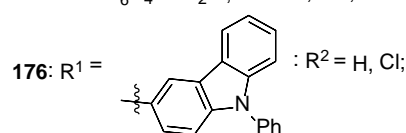
**172:** R<sup>2</sup> = H, R<sup>1</sup> = *o*-C<sub>6</sub>H<sub>4</sub>;

**173:** R<sup>2</sup> = Cl, R<sup>1</sup> = H



**174:** R<sup>2</sup> = H, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>X-4 (X = H, Me, Bu<sup>t</sup>, SMe, OMe, NMe<sub>2</sub>);

**175:** R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-4; R<sup>2</sup> = Cl, CN;

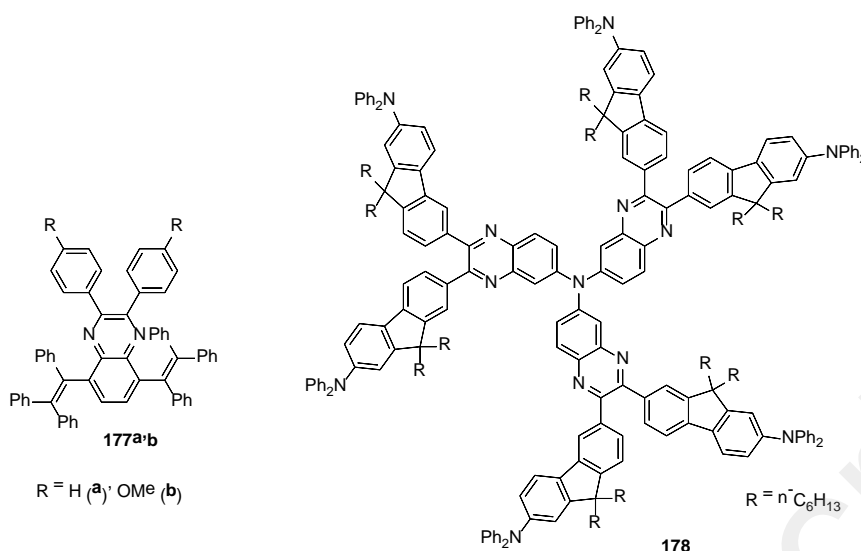


TMS = SiMe<sub>3</sub>

Wang *et al.* have synthesized chromophores **177a,b** that exhibit aggregation-enhanced emission in MeCN/water mixture and selective fluorescent quenching toward picric acid.<sup>135</sup>

Lin *et al.* have designed star-shaped chromophore **178**.<sup>116</sup> This compound exhibits emission at 498 nm in toluene (Φ<sub>F</sub> = 0.42) and TPA properties with TPA cross section as high as 8950 GM at 790 nm.

### Structures 177, 178



Kim and coworkers have designed fluorene-bridged quinoxaline derivative **179**.<sup>111</sup> As its quinazoline analogue **140**, this compound exhibits blue luminescence in DCM solution and thin film. A blue OLED with external quantum efficiency of 1.30% (slightly lower than with **140**) has been obtained with this compound.

Yu *et al.* have described two fluorine substituted quinoxaline chromophores **180a,b** that exhibit aggregation-induced emission (AIE) and thermally activated delayed fluorescence (TADF).<sup>136</sup> Compound **180a** exhibits 23.5% efficiency (EQE) in doped OLED and 10% efficiency in non doped orange OLED.

Nowadays much attention is paid to 2,3-diphenylquinoxaline derivatives as electron-acceptors for emitters exhibiting TADF effect; such materials are particularly perspective for OLED due to their theoretical ability to reach 100% of internal quantum efficiency via reverse intersystem crossing (RISC) between singlet and triplet states. Compound **181**, which contains a fluorine-substituted quinoxaline as an electron-acceptor and phenoxazine with good hole-transporting ability as an electron-donor, was described.<sup>137</sup> Synthesis of **181** was realized by Pd-catalyzed C-N coupling reaction of 6,7-difluoro-2,3-diphenylquinoxaline with phenoxazine. The product **181** demonstrated good thermal stability with a high decomposition temperature of 348 °C and a broad and weak absorption around 400–500 nm. The neat film of **181** exhibited a bright orange/red emission peak at 606 nm, phosphorescence spectra with a maximum peak at 616 nm was recorded in the neat film at 77 K. According to the fluorescence and phosphorescence spectra, the energetic gap  $\Delta E_{\text{ST}}$  between first singlet excited state S1 and first triplet excited state T1 of **181** is estimated to be 0.04 eV, which is favourable for efficient RISC. Phenoxazine-containing quinoxaline **181** proved to be long-wave TADF emitter, OLED based on **181** achieved a maximum EQE of 13.9% or 9.0% depending on the way of its fabrication.

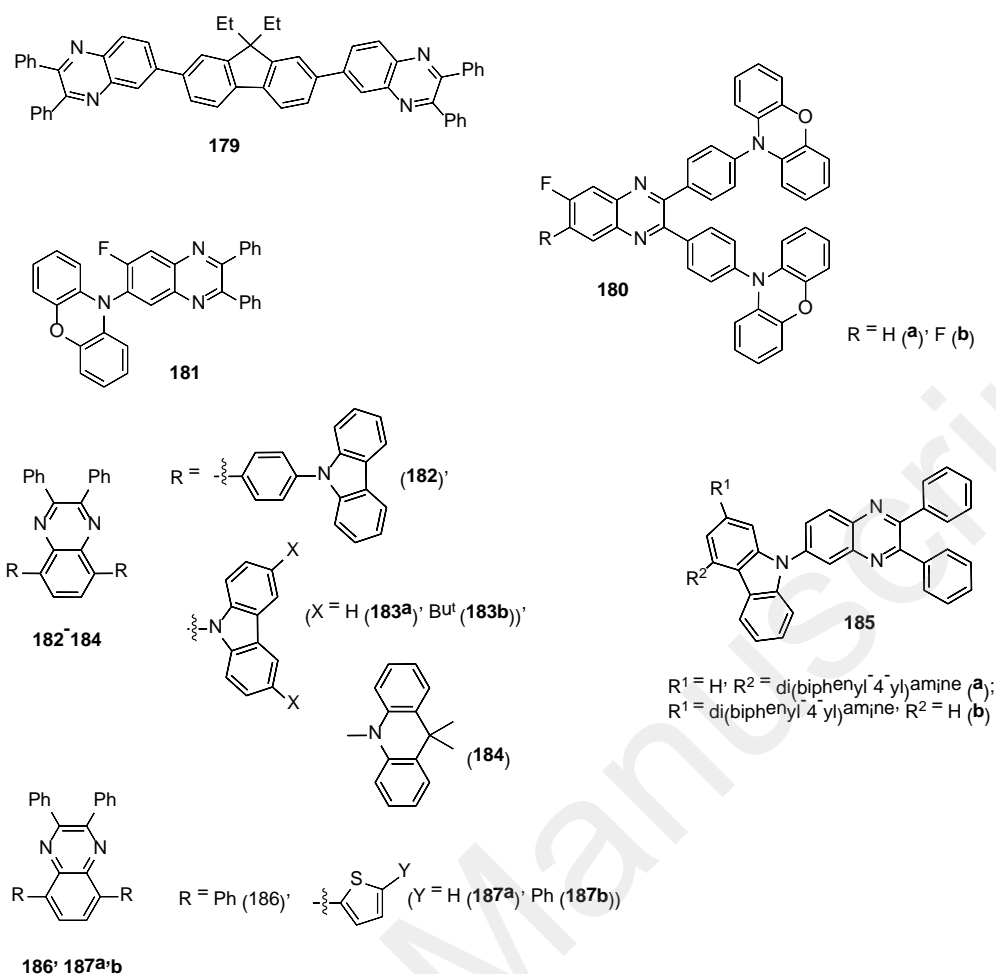


A series of new butterfly-shaped D-A-D type compounds **182-184** with quinoxaline as an electron acceptor and carbazole or dihydroacridine residues as electron donors was presented by the same Yu's scientific group.<sup>138</sup> These derivatives were synthesized from 5,8-diphenylquinoxaline using Pd-catalyzed C-N cross-coupling reaction, Suzuki process or copper-catalyzed Ullmann coupling reaction. All compounds exhibit excellent thermal stability with 5% weight loss decomposition temperatures ( $T_d$ ) in the range of 394-471 °C. Electrochemical and photophysical properties of **182-184** were studied. It was shown that with the increasing electron-donating ability from phenyl to carbazole and dihydroacridine, the ICT absorption bands gradually red-shift from 370 nm (**182**) to 482 nm (**184**). In films all compounds exhibit luminescence from green to orange with  $\lambda_{em}$  from 502 nm (**182**) to 603 nm (**184**). Phosphorescence spectra were recorded in order to estimate  $\Delta E_{ST}$  value which ranges from 0.07 eV (**184**) to 0.33 eV (**182**) and was found to be in agreement with results of the theoretical analysis. Authors successfully tuned the emission type from local excited-state (LE) to charge-transfer state (CT) transition to acquire a TADF molecule. Although the **184**-based orange TADF device exhibited an EQE of only 7.4%, the contribution from the delayed fluorescence to the overall EQE can reach up to 97%.

Two novel quinoxaline derivatives **185a,b** bearing disubstituted carbazole fragment also exhibit TADF emitter properties.<sup>139</sup> Authors demonstrated that the degree of planarity of emitter molecule has a decisive influence on its electroluminescence properties. The influence of structure of compounds **185** on molecular orientation in films and mixtures containing bis(2-(diphenylphosphino)phenyl)ester (DPEPO) and the electroluminescence properties in TADF OLEDs has been studied. Compounds **185** were found to possess green fluorescence in films at room temperature with  $\lambda_{em}$  = 517 nm (**185a**) and 546 nm (**185b**), luminescence quantum yield 60.4% and 50.2% respectively and the value of  $\Delta E_{ST}$  0.10 (**185a**), 0.12 (**185b**). More horizontal molecular orientation of **185** was observed in the mixtures of compounds (in 6 mass% concentrations) and DPEPO in comparison with neat films that influence positively on OLED performances. The maximum electroluminescence external quantum efficiency measured in the device based on **185b** was found to be 15.4 %.

Kim *et al.* have incorporated compounds **186, 187** as organic semiconductors in top-contact/bottom-gate organic thin-film transistors (OTFTs).<sup>140</sup> Thin film of **187b** showed p-channel characteristics with hole mobilities as high as  $2.6 \cdot 10^{-5}$  cm<sup>2</sup>/Vs and current on/off ratio of  $3.5 \cdot 10^6$  via vacuum deposition.

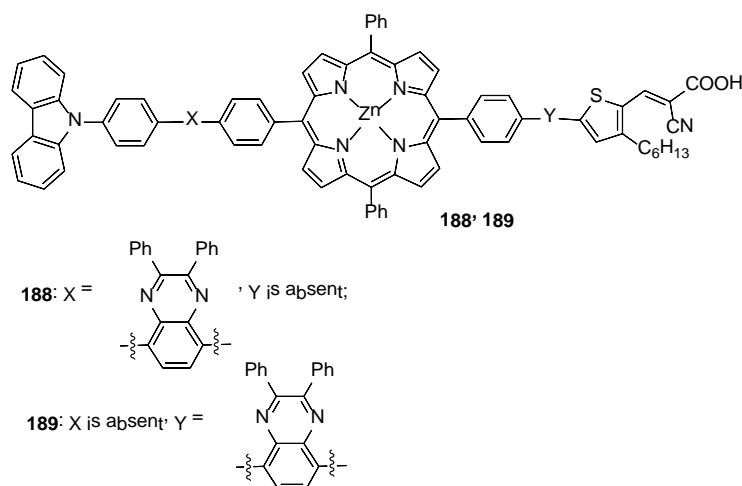
## Structures 179-187



The quinoxaline fragment has been extensively used in organic photovoltaic (OPV). In particular the diphenylquinoxaline unit has shown a great potential in anti-aggregation and broadening spectra response.<sup>141</sup> The recent developments of quinoxaline derivatives for photovoltaic have been recently reviewed<sup>142-144</sup> and structures presented in these reviews will not be discussed here.

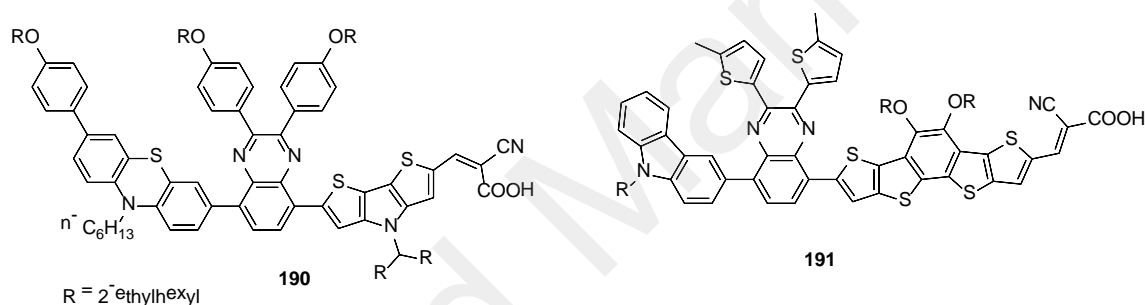
Fan and coworkers have designed sensitizers **188** and **189**.<sup>145</sup> In these structures, the 2,3-diphenylquinoxaline fragment acts as an auxiliary acceptor. Whereas the incorporation of this fragment between the donor and porphyrin unit (**188**) has negligible influence on the absorption property, its incorporation between the porphyrin unit and acceptor (**189**) significantly increases the absorbance for the Soret band and valley between Soret and Q bands. The quasi solid state DSSC with **189** displays a PCE of 6.02%, 51% higher than those for **188**.

### Structures 188, 189



Han *et al.* have designed phenothiazine chromophore **190**.<sup>146</sup> DSSC based on this compound exhibits an excellent PCE of 10.06%. Zhang *et al.*<sup>147</sup> have designed dye **191** for DSSC application. DSSC device with PCE of 4.63% was obtained.

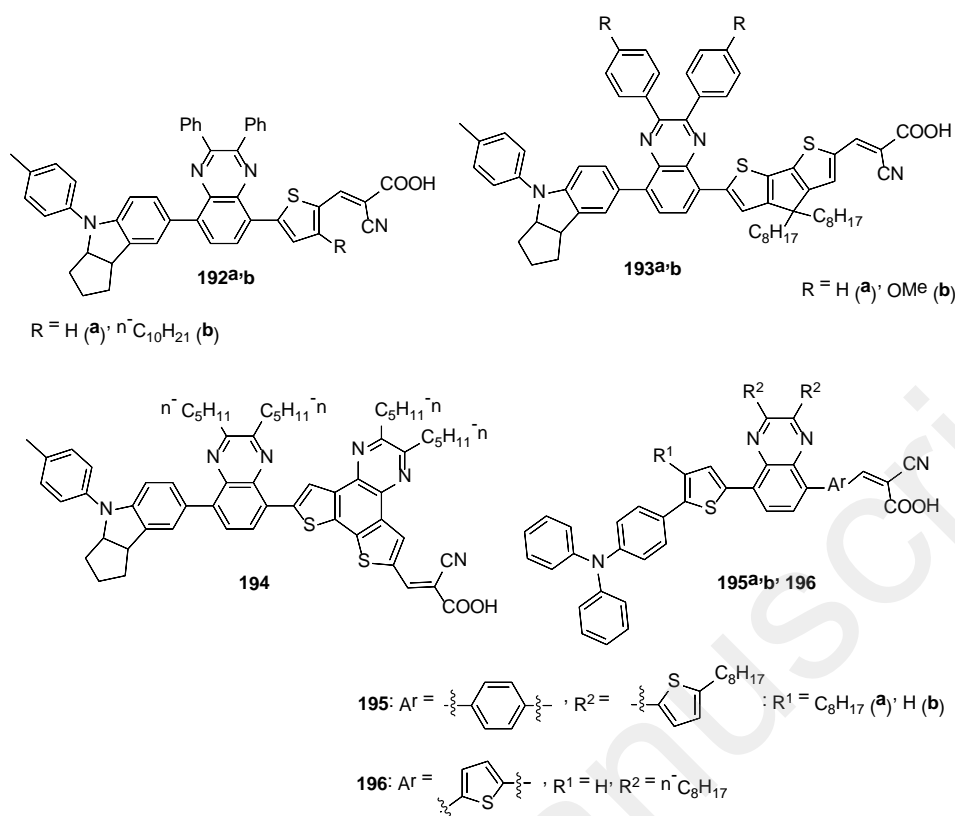
### Structures 190, 191



Pei and coworkers and Wang *et al.* have described D-A- $\pi$ -A chromophores **192a,b**, **193a** as solar cell sensitizers.<sup>125,148</sup> The two phenyl groups grafted onto the quinoxaline core are demonstrated as efficient building block by improvement of photostability and thermal stability and as antiaggregation functional unit and appear as an alternative to stability deleterious alkyl chain grafted thienyl bridge. Dyes **192b** and **193a** exhibit conversion efficiency as high as 9.24% and 8.76% respectively. Compound **193b** with methoxy substituent on the phenyl fragment was designed by Xu *et al.*<sup>149</sup> and DSSC with this sensitizer exhibits a PCE of 9.83%.

Ji and coworkers have shown that the addition of a 2,3-di-*n*-pentylquinoxaline as auxiliary acceptor in sensitizer **194** significantly enhances photovoltaic performance with PCE of 7.98%.<sup>150</sup>

### Structures 192-196

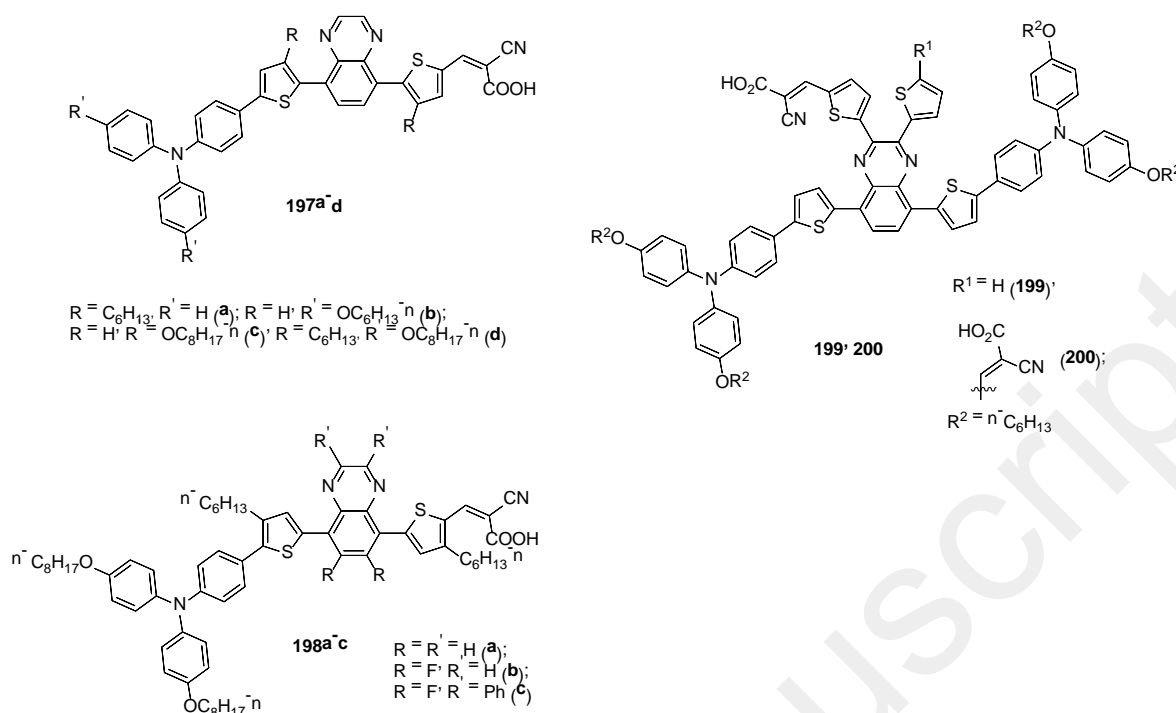


Godfroy and coworkers have synthesized D- $\pi$ -A- $\pi$ -A organic sensitizer **195a**.<sup>151</sup> DSSC based on **195a** shows a PCE of 6.36%. DSSC obtained from similar structures **195b** and **196** designed by Ma *et al.*<sup>152</sup> exhibit PCE of 7.29 and 7.78% respectively.

Lu *et al.* have described a series of quinoxaline chromophores **197a-d** for DSSCs.<sup>153</sup> When the alkyl substituent are removed from the spacer part in **197a** to the donor part in **197b** and **197c** a more conjugated system and a bathochromically shifted maximum absorption band can be realized. Based on **197d** quasi solid state DSSC exhibits a power conversion efficiency of 7.14% (8.27% with liquid electrolyte). This sensitizer can be combined with another phenazine-based sensitizer with complimentary absorption profile and PCE of 8.04% in quasi solid state DSSC has been achieved.<sup>154</sup>

The incorporation of fluorine atom has been also tested on similar structures **198b** and **198c**.<sup>155</sup> When compared with unsubstituted analogue **198a**, the quasi-solid state DSSC based on **198c** exhibits a 37% higher efficiency (PCE of 8.2% for **198a**).

## Structures 197-200



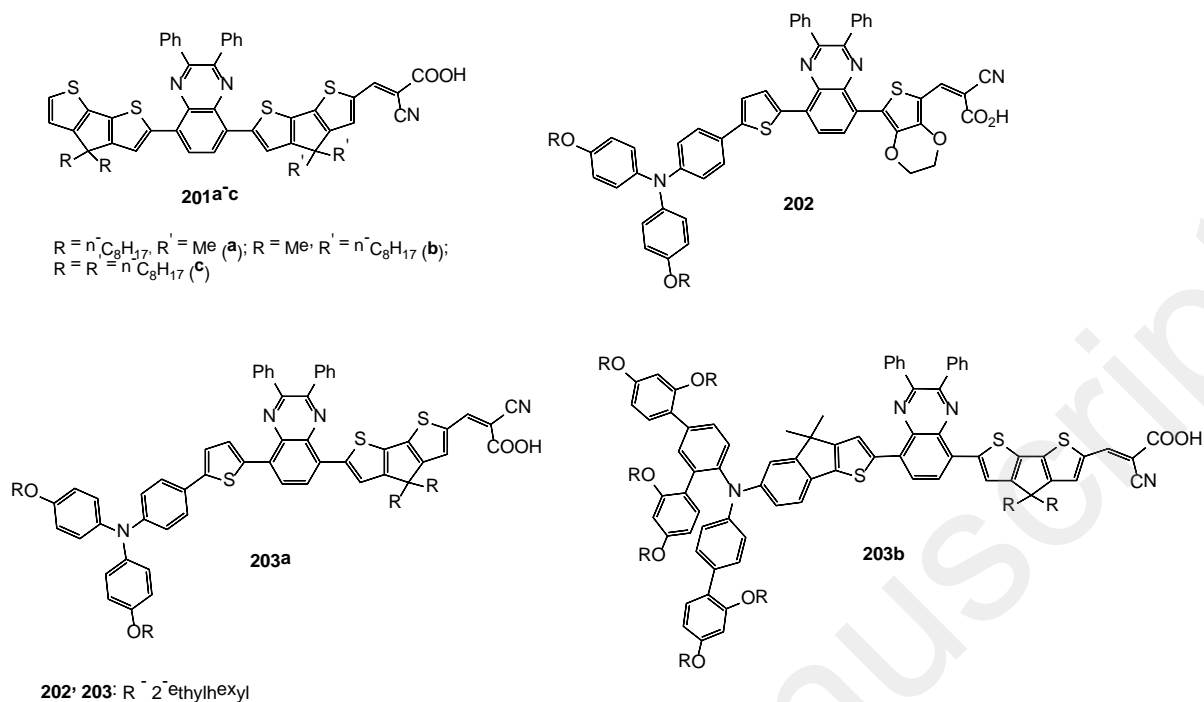
The same team has also designed sensitizers **199** and **200**.<sup>156</sup> A broader and more intense charge transfer band is observed for **199** with a single anchoring group that exhibits a power conversion efficiency of 5.2% for a quasi-solid-state DSSC (6.2% with liquid electrolyte) with good stability.

Shen and coworkers have designed sensitizers **201a-c**.<sup>157</sup> They have demonstrated that the incorporation of electron-deficient quinoxaline into the  $\pi$ -chain significantly enhances the PCE (20% increase) and DSSC based on **201a** exhibits the best performance (PCE of 8.05%).

Li *et al.* have designed two D-A- $\pi$ -D sensitizers **202** and **203a** employing 3,4-ethylenedioxythiophene and cyclopentadithiophene as  $\pi$ -linker respectively.<sup>158</sup> Compounds **202**, **203a** were obtained from 5,8-dibromo-2,3-diphenylquinoxaline via sequenced reactions of Stille cross-coupling, formylation, substitution of second bromine with (diarylamino)phenylthiophene fragment and condensation with 2-cyanoacetic acid. 2,3-Diphenyl-5,8-dithienylquinoxalines **202**, **203a** possess intensive absorption in DCM in visible range ( $\lambda_{abs} = 553$  nm,  $\epsilon = 1.75 \cdot 10^4$  M<sup>-1</sup>cm<sup>-1</sup> for **202** and  $\lambda_{abs} = 569$  nm,  $\epsilon = 4.12 \cdot 10^4$  M<sup>-1</sup>cm<sup>-1</sup> for **203a**). When grafted on TiO<sub>2</sub>, blue shift of absorption band was observed with maxima  $\lambda_{abs} = 534$  and 537 nm respectively for **202** and **203a**. An all-solid state DSSC with **203a** has been obtained with an impressive PCE of 8.0%.

New blue dye **203b**, bearing 2,3-diphenylquinoxaline as acceptor, indeno[1,2-*b*]thiophene-functionalized triethylamine as donor and cyclopentadithiophene as  $\pi$ -linker, was synthesized by the same method as quinoxalines **202**, **203a**. Compound **203b** exhibits wide absorption band with  $\lambda_{abs} = 600$  nm and high extinction coefficient ( $\epsilon = 6.3 \cdot 10^4$  M<sup>-1</sup>cm<sup>-1</sup>). DSSC device fabricated on the basis of **203b** demonstrated high efficiency (PCE = 7.81%).<sup>159</sup>

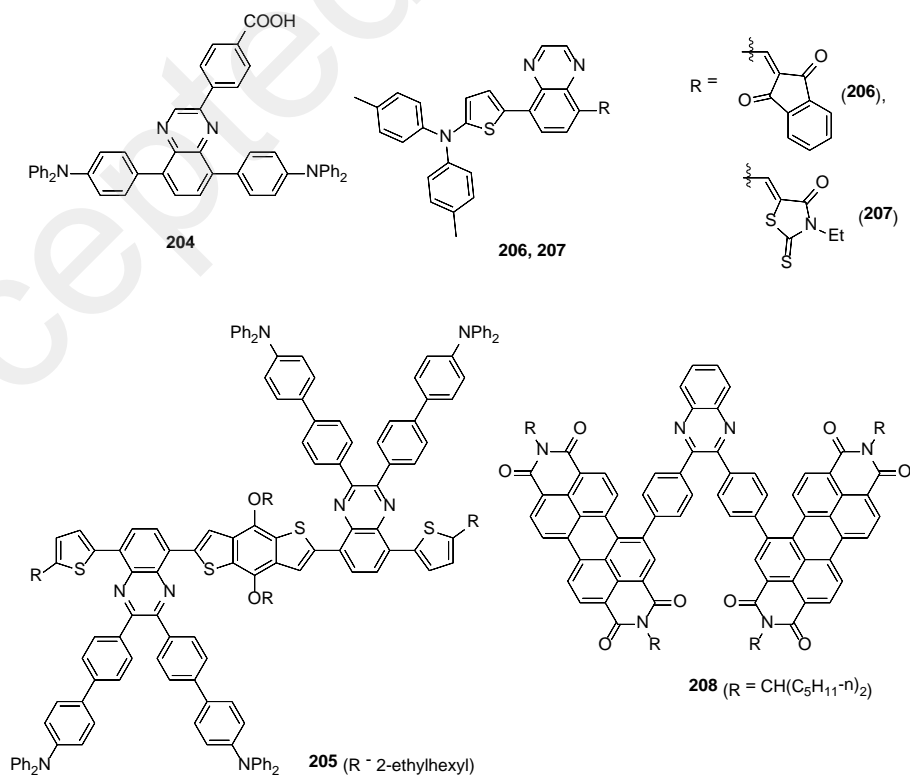
## Structures 201-203



Kono and coworkers have designed sensitizer **204**.<sup>160</sup> DSSCs with **204** showed PCE of 3.2%. To improve the device performances, thienopyrazine analogue was used as a co-adsorbent and PCE of 6.2% was achieved.

Yu *et al.* have designed sensitizer **205** that can be used in solution-processed organic photovoltaic devices with PCE of 1.22%.<sup>161</sup>

## Structures 204-208

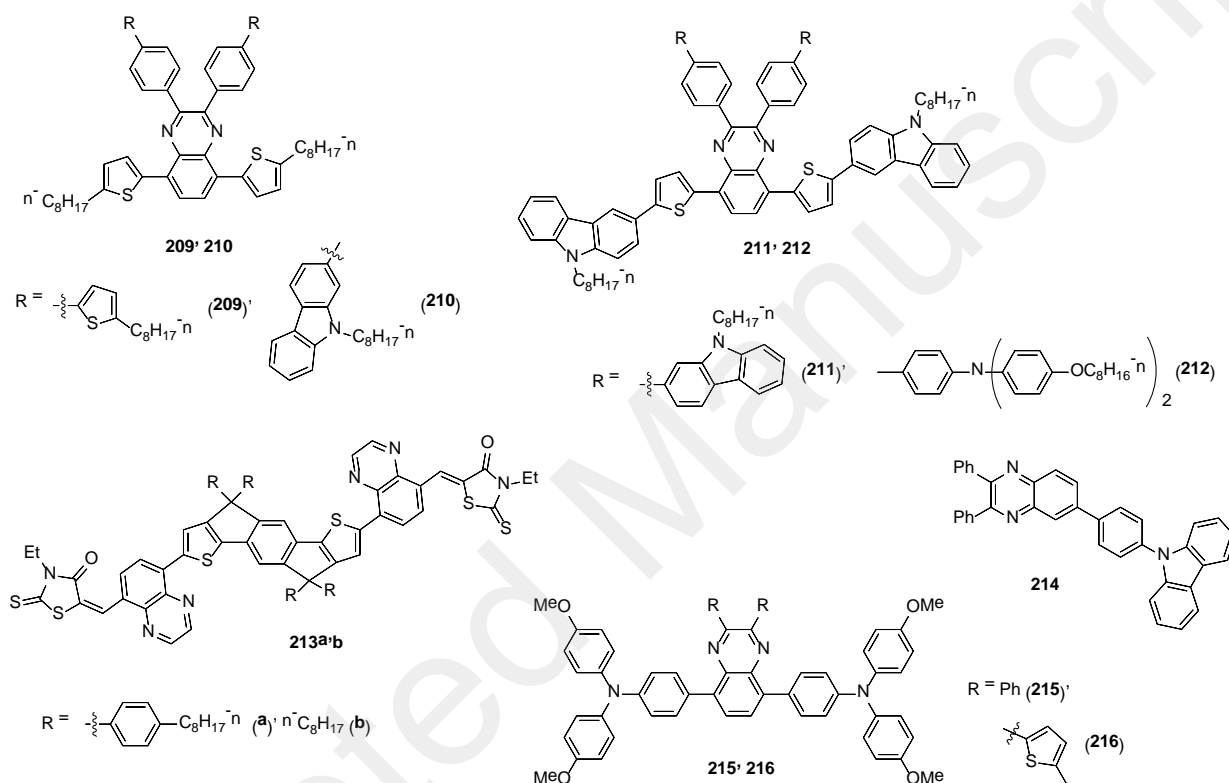


Qi *et al.* have designed chromophores **206** and **207** as donors for bulk-heterojunction solar cells.<sup>162</sup> With the configuration FTO/c-TiO<sub>2</sub>/**206** or **207**: C<sub>70</sub>/MoO<sub>3</sub>/Ag, bulk-heterojunction solar cells with PCE of 1.44 and 1.70% were obtained respectively.

Liu and coworkers have studied perylenediimide acceptor **208**. Based on **208** non-fullerene photovoltaic device has been obtained and show PCE of 3.86%.<sup>163</sup>

Deng and coworkers have designed chromophores **209-212** based on quinoxaline as potential donor for bulk-heterojunction organic solar cells.<sup>164</sup>

### Structures 209-216



Xiao and coworkers have described A<sub>2</sub>-A<sub>1</sub>-D-A<sub>1</sub>-A<sub>2</sub> chromophores **213a,b** where the quinoxaline is used a bridge acceptor (A<sub>1</sub>) fragment.<sup>165</sup> These sensitizers exhibit the complimentary absorption spectra with poly(3-hexylthiophene) (P3HT) and polymer solar cells based on P3HT:**213a** and P3HT:**213b** showed power conversion efficiency of 4.03 and 4.81% respectively.

9-(4-(2,3-Diphenylquinoxalin-6-yl)phenyl)-9H-carbazole (**214**) was designed as host material for red phosphorescence OLED, which demonstrated outstanding electroluminescence performance with maximum current efficiency 21.9 cd/A, power efficiency 15.4 lm/W and external quantum efficiency 12.2%.<sup>166</sup>

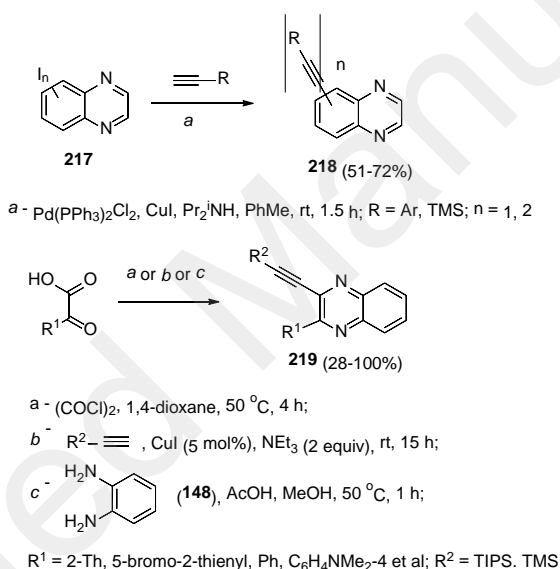
Zhang and coworkers have designed D-A-D hole transporting materials **215** and **216** based on quinoxaline central core for perovskite solar cells.<sup>167</sup> Based on **216**, perovskite solar cells exhibit

a maximum efficiency of 19.62% outperforming the spirobifluorene derivative generally used as hole transporting material.

## II.2.6. Arylethynylquinoxalines

Arylethynylquinoxalines derivatives are generally obtained by Sonogashira cross coupling reaction. 2-Arylethynylquinoxalines and 2,3-diarylethynylquinoxalines can be obtained from chloro derivatives.<sup>168</sup> On the other hand, 6-arylethynylquinoxalines and 5,8-diarylethynylquinoxalines **218** have been obtained from iodo derivatives **217** (Scheme 17, top reaction).<sup>127,169</sup> Another strategy to obtain 2-aryl-3-ethynylquinoxaline **219** based on three-component activation/alkynylation/cyclocondensation (AACC) process has been recently proposed (Scheme 17, bottom reaction).<sup>134</sup>

**Scheme 17**



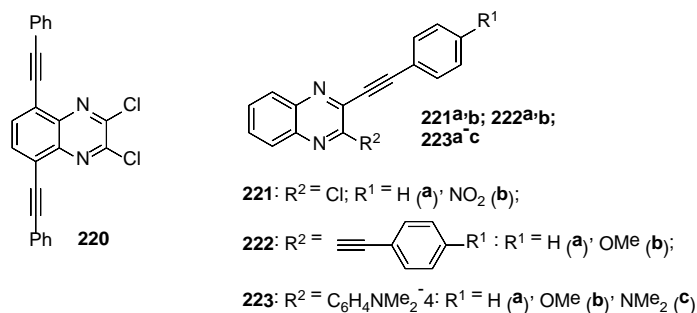
Nafe *et al.* have synthesized 5,8-di(phenylethynyl)quinoxaline **220**. This compound exhibits red-shifted emission ( $\lambda_{\text{em}} = 483 \text{ nm}$ ) and increased fluorescence quantum yield ( $\Phi_{\text{F}} = 0.85$ ) with regards to diphenyl analogue **153**.<sup>127</sup>

Nguyen *et al.* have studied the photophysical properties of compounds **221**, **222**.<sup>167</sup> Whereas 2-phenylethynylquinoxalines **221a,b** exhibit UV-emission ( $\lambda_{\text{em}} = 386\text{--}395 \text{ nm}$ ), disubstituted quinoxalines **222a,b** show purple emission ( $\lambda_{\text{em}} = 425\text{--}445 \text{ nm}$ ).

Merkt and coworkers have designed 2-aryl-3-arylethynylquinoxalines **223**.<sup>134</sup> These compounds exhibit yellow-orange emission ( $\Phi_{\text{F}} = 0.23\text{--}0.42$ ) in DCM with blue shifted emission when the electron-donating strength of the substituent of the phenylethynyl fragment is increased (**223a**:  $\lambda_{\text{em}} = 596 \text{ nm}$ , **223b**:  $\lambda_{\text{em}} = 586 \text{ nm}$ , **223c**:  $\lambda_{\text{em}} = 574 \text{ nm}$ ).

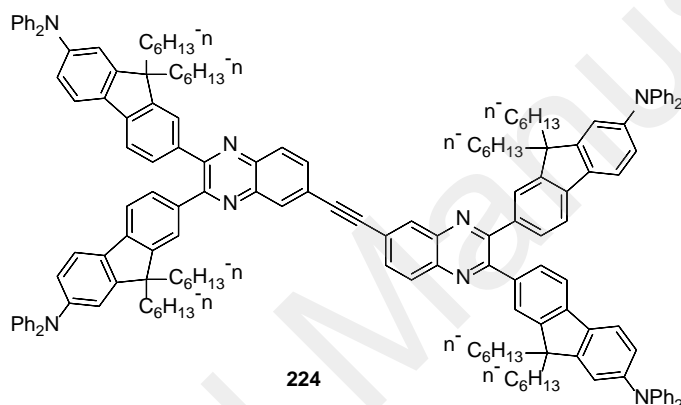
## Structures 220-223





Lin and coworkers have designed bisarylacetylene derivative **224** as two-photon absorption chromophore.<sup>169</sup> A two photon cross section of  $\sim 2000 \text{ GM}$  at 730 nm, higher than that of vinylene analogue **74a**, has been observed in toluene.

**Structure 224**



As shown by these numerous examples, the design of (het)aryl- and (het)arylethynylbenzo(di)azine has been a really active field of research during the last seven year. These chromophores have found applications in various field such as bioimaging, OLEDs, photovoltaism.

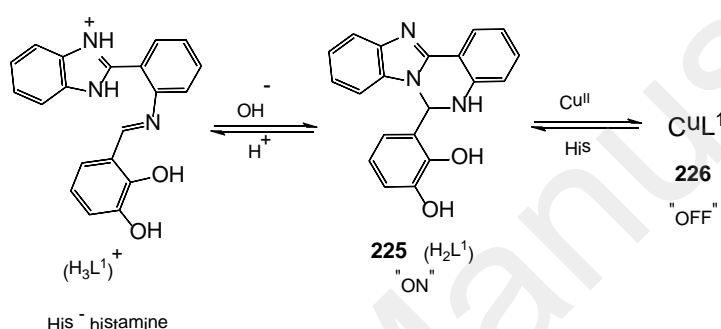
### III. Annelated benzazines

Different annelated derivatives of quinazolines and quinoxalines are presented in reviews.<sup>23,170</sup> Many derivatives of annelated benzazines found application as ligands for the synthesis of metalcomplexes. For example, benzo[*h*]quinoline,<sup>171,172</sup> and 4-arylthieno[3,2-*c*]quinoline<sup>173</sup> are used as cyclometallating ligands with expanded  $\pi$ -conjugated system. Derivatives of dipyrido[3,2-*f*:2,3-*h*]quinoxaline (dpq) are applied for the complexation with wide range of metals,<sup>174-176</sup> in particular, for obtaining complexes with rare-earth elements in which ligand acts as effective antenna.<sup>177</sup>

Wang and co-authors described 6-(2,3-dihydroxyphenyl)-5,6-dihydrobenzimidazo[1,2-*c*]quinoline **225**, obtained from 2-(2-aminophenyl)benzimidazole and 2,3-dihydroxybenzaldehyde

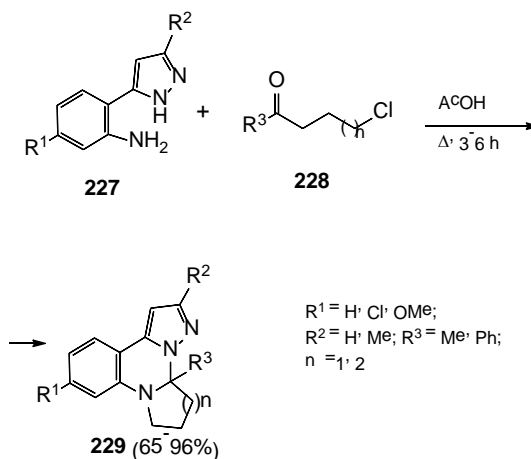
by boiling in methanol for 24 h.<sup>178</sup> The structure of compound **225** was confirmed by X-ray method. This ligand ( $H_2L^1$ ) exhibited strong emission at 434 nm in the mixture DMSO/water. Mixing of **225** with different metal ions demonstrated that only addition of Cu(II) ions lead to luminescence quenching in the ratio  $H_2L:Cu(II) = 1:1$ . Authors showed that complex **226** forms with azomethine intermediate ( $H_3L^1$ ) into which ligand **225** transforms at pH below 5 (Scheme 18). The addition of histidine to the complex **226** led to considerable increase of emission at 434 nm due to ligand substitution. Thus, authors presented compound **225** as fluorescent hemosensor for selective detection of Cu (II), including in physiological media, and complex **226** can be applied for the detection of histidine.

Scheme 18



Acosta and co-authors reported the new series of pyrazolo[1,5-*c*]pyrrolo[1,2-*a*]quinazolines and pyrazolo[1,5-*c*]pyrido[1,2-*a*]quinazolines **229**, synthesized by the cascade reaction of anilines **227** and  $\omega$ -chloroketones **228** (Scheme 19).<sup>179</sup> These compounds demonstrated mainly blue or green luminescence. Emission spectra of **229** in chloroform exhibited two bands at 358–448 nm and 386–482 nm, attributed to associated and non-associated compounds in non-polar solvent. In ethanol, polar hydrogen-bonding solvent, emission spectra have one band at 382–409 nm, attributed to non-associated compounds. Notably, the luminescence quantum yields for these compounds are rather high ( $\Phi_F = 0.63$ – $0.13$ ). Studying of electrochemical properties of compounds **229** showed that they can be oxidized chemically into completely  $\pi$ -conjugated systems.

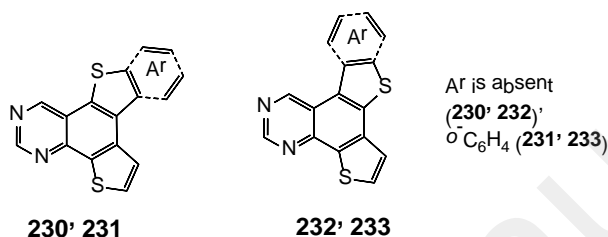
Scheme 19



Annelated dibenzo- and phenanthroline- quinazoline derivatives were described in patents<sup>180,181</sup> as emitting, electron-transport and hole-transport layers for OLEDs. Derivative of dibenzo[*f,h*]quinoxaline were patented as emitting elements in light-emitting materials and devices.<sup>182</sup>

Synthesis and photophysical properties of new dithienylquinazolines **230-233** are described.<sup>183,184</sup> Compounds were obtained by oxidative cyclization of the correspondent 4,5-dithienylpyrimidines, they exhibit blue fluorescence ( $\lambda_{em} = 388-417$  nm) with quantum yield in the range of 1.8-4.1%.

#### Structures 230-233

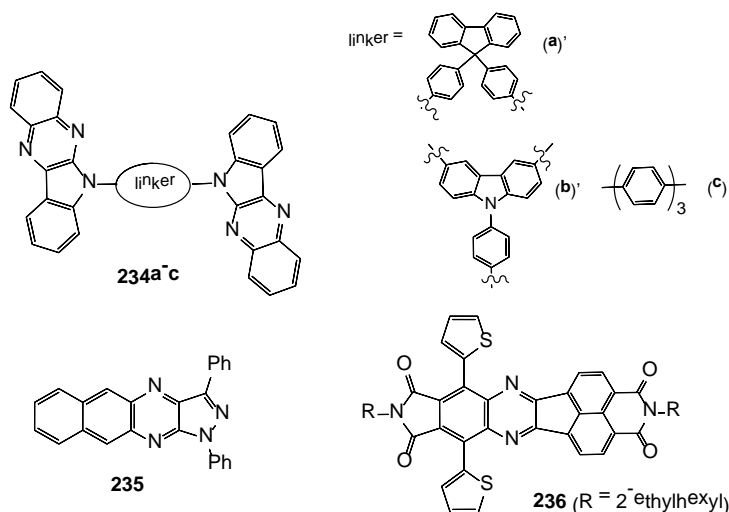


Three novel bis(6*H*-indolo[2,3-*b*]quinoxaliny) derivatives **234a-c** containing fluorenyl, terphenyl or carbazole bridge were described as emitters for phosphorescent OLEDs.<sup>185</sup> In toluene solution at room temperature these compounds exhibit fluorescence with  $\lambda_{em} = 470-500$  nm, in thin film emission maxima were observed at 487–525 nm. At 77 K in thin film phosphorescence with  $\lambda_{em} = 543-594$  nm was noted. Electroluminescent devices based on these materials and iridium additives demonstrated deep red emission and showed EQE > 20%.

1,3-Diphenyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]quinoxaline **235**, obtained from 2,3-diaminonaphthalene and 2,5-diphenylpyrazol-3,4-dione exhibited photoluminescence in THF solution with  $\lambda_{em} \sim 580$  nm.<sup>186</sup> The electronic device fabricated on the basis of **235** demonstrated yellow emission with  $\lambda_{em} = 548$  nm and brightness 800 cd/m<sup>2</sup>.

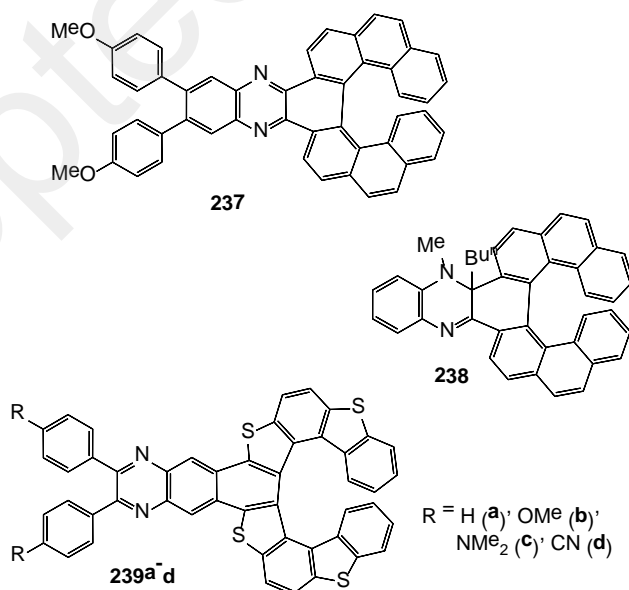
Lan and co-authors reported acenaphtho[1,2-*b*]quinoxalin-diimide **236** as potential non-fullerene component for organic solar cells.<sup>187</sup> This compound demonstrated relatively wide absorption band (from 300 to 650 nm) with moderately low-lying LUMO level (-3.64 eV) and average optical gap ~2 eV.

#### Structures 234-236



Sakai and co-authors reported quinoxaline[7]carbohelicene derivatives **237**, **238** as quinoxaline-containing nonplanar molecular systems possessing luminescent properties.<sup>188,189</sup> Compound **237** and unsubstituted quinoxalin[7]carbohelicene were synthesized from carbohelicene diketone and the corresponding 1,2-diaminobenzene. In order to obtain 1,2-dialkylsubstituted **238** quinoxaline fragment was reduced with dithionite, then reaction with butyllithium and methyl iodide was performed.<sup>187</sup> Both structures were characterized by spectral methods including X-ray. Compound **237** exhibited fluorescence in THF solution with  $\lambda_{em} = 550$  nm and  $\Phi_F = 0.05$ .<sup>188</sup> In crystals the second band also was observed at 590 nm which can be attributed, according to authors, to the exumer-like delocalized excited state.

### Structures 237-239



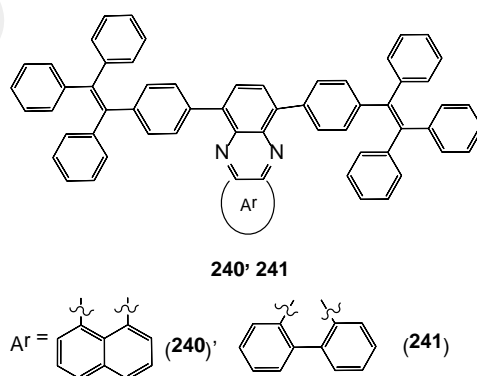
Compound **238** demonstrated red shift of emission band in comparison with quinoxalin[7]carbohelicene approximately at 100 nm (yellow fluorescence) and five-fold increase

in quantum yield ( $\Phi_F = 0.25$ ) relatively to **237**. Circularly polarized luminescent (CPL) properties were studied, OLED based on derivative **238** as emitting layer was successfully fabricated.

The same group of authors<sup>190</sup> obtained the series of fluorescent «push-pull» tetrathia[9]helicenes **239**, bearing quinoxaline as acceptor fragment. Compounds were characterized by NMR  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as well as MALDI-TOF and ESI-QTOF mass-spectrometry data. Compounds **239** exhibit strong fluorescence in THF solution with  $\lambda_{\text{em}} = 600\text{--}660$  nm depending on the nature of substituent R, higher quantum yield ( $\Phi_F = 0.43$  for **239c** and 0.30 for **239d**) and large Stokes shift. Increased value of  $\Phi_F$  for compound **239d** allowed to get information on CPL properties, the degree of anisotropic factor was estimated ( $g_{\text{CPL}} = 3.0 \cdot 10^{-3}$ ). Incorporation of quinoxaline into tetrathio[9]helicene core promotes the «push-pull» nature of thiahelicene derivatives.

New T-shaped tetraphenylethylene-substituted derivatives of acenaphthene- and phenanthrene-quinoxaline **240**, **241** with D-A-D structure were reported.<sup>191</sup> Both luminophores were synthesized by Suzuki cross-coupling reaction from quinoxaline dibromoderivative and boronic acids. Compounds exhibit fluorescence in solution, which is sensitive to solvent polarity: derivative **240** demonstrated blue emission in toluene with  $\Phi_F = 0.18$  and green emission in dichloromethane with  $\Phi_F = 0.33$ , whereas its counterpart **241** demonstrates green emission in toluene with  $\Phi_F = 0.21$  and yellow emission in dichloromethane with  $\Phi_F = 0.55$ . Studying of fluorescent properties of these compounds in the THF-water mixture showed that **240**, **241** exhibit aggregation induced emission. In solid state luminophores **240**, **241** demonstrated reversible mechanochromism with good color contrast due to morphological change from crystal to amorphous state.

#### Structures 240, 241

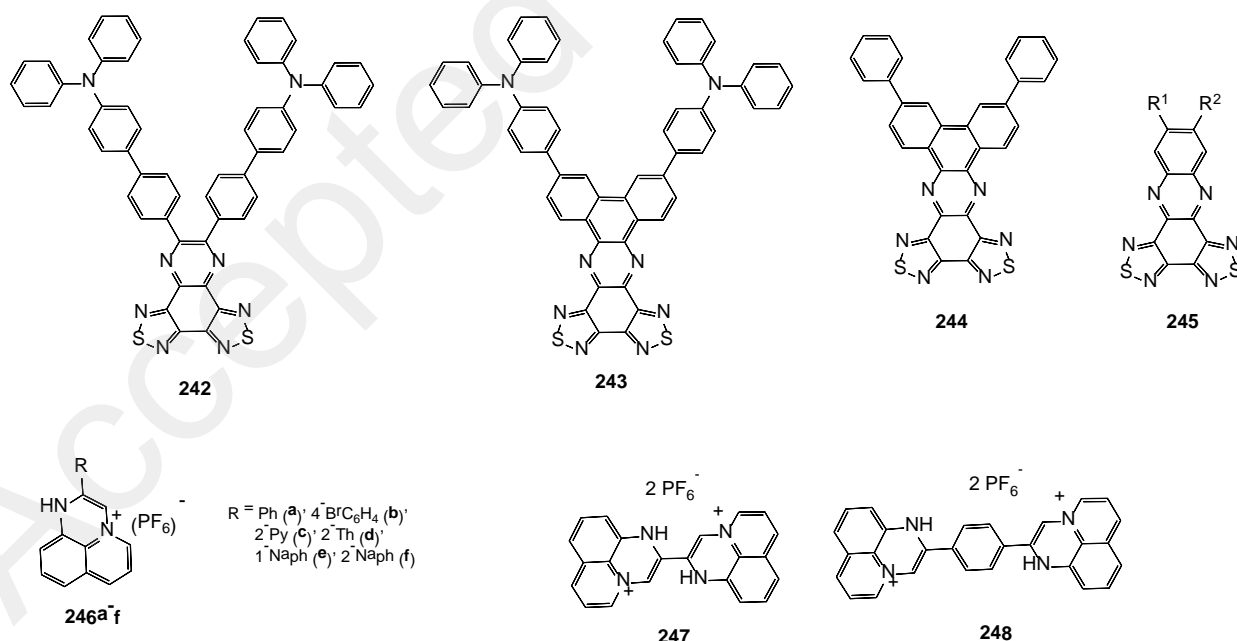


V-shaped fluorescent dyws of D-A type **242-244** bearing bis(thiadiazol)quinoxaline and bis(thiadiazol)phenanthroquinoxaline were described.<sup>192</sup> In solution, the luminescence and red shift of emission band as well as decrease in intensity were observed with the growth of solvent polarity (for compound **242**  $\lambda_{\text{em}}$  changed from 474 nm in cyclohexane to 652 nm in DCM,  $\Phi_F$  from 0.36 to

0.03; for compound **243**  $\lambda_{em}$  changed from 484 nm to 678 nm,  $\Phi_F$  from 0.51 to 0.11). Derivative **244** with lack of donor fragment did not show the dependence of emission on solvent polarity. In solid state orange emission was observed for compound **243** with  $\Phi_F = 0.17$ , for **242** emission was weaker ( $\Phi_F = 0.03$ ) and for **244** it was practically absent. Emission behavior of compounds **242-244** was studied in the mixture THF-water, the most distinct changes were observed for compound **243**. At 0% of water fraction this derivative emitted red light with  $\lambda_{em} = 654$  nm and  $\Phi_F = 0.23$ , when increasing the water fraction up to 30% the intensity considerably decreased, having reached  $\Phi_F = 0.002$ . However, beginning from 40% of water the intensity of emission increased with the final value  $\Phi_F = 0.18$  at 90% and hypsochromic shift to orange range is observed. At the high content of water compound **243** formed aggregates due to hydrophobic interaction which create the hydrophobic space limiting polarization of the excited state and, as a result, quenching of emission. Transition from initial condition of emission to final through intermediate quenching, reached in V-shaped structure of compound **243**, was shown as an example of creation of emission system in the polar water medium. According to authors, unusual double change of emission is caused by the combined aggregation effect and twisted ICT.

Derivatives of bis(thiadiazol)quinoxaline of general formula **245** were patented as organic light emitting elements and materials.<sup>193</sup> It worth to note that organic dyes emitting in red and near IR range are most important for biovisualization and biological studies.

#### Structures 242-248



Laramée-Milette and co-authors obtained the series of 1H-pyrido[1,2,3-de]quinoxaline cationic dyes **246-248** by the reaction of 8-aminoquinoline with  $\alpha$ -bromoketone.<sup>194</sup> The structure of compounds **246a,b** was confirmed by X-ray data. The majority of derivatives exhibit luminescent

properties in solution and solid state with  $\lambda_{em} = 500\text{--}700$  nm and low quantum yield ( $\Phi_F = 0.005\text{--}0.017$  in MeOH). The exception made the compound **247** which proved to be non-emissive in solid state. On the basis of the conducted researches authors came to the conclusion that the observed luminescence in solid state for compounds **246**, **248** can be caused by strong intermolecular  $\pi\text{-}\pi$  interaction leading to aggregation induced emission.

#### IV. Polymer benzazines

Functionalised benzazines are included into various  $\pi$ -conjugated polymers which are perspective for application in different spheres as photoactive materials. Among them quinoxaline and its derivatives have been widely used as building blocks because they can be easily modified by varying the side chains, that promotes the creation of polymeric products. Thus, recent reviews<sup>142-144</sup> are devoted to the development of quinoxaline based polymers for organic photovoltaics (OPV).

Gedefaw and co-authors collected data on the basic structure of monomer quinoxalines and their incorporation into the conjugated polymers of D-A type, special attention was paid to a combination of quinoxaline and benzothiophene fragments in polymeric chain.<sup>142</sup> A broad range of structures and devices considered in this work showed a possibility of precise control of quinoxaline-containing polymers properties for the creation of highly effective OPV devices due to high stability, universality, mild and inexpensive synthesis, peculiar optical, chemical and electronic properties of quinoxaline as acceptor building-block in D-A polymers.

Yuan and co-authors focused on design and synthesis of photovoltaic polymers, including quinoxaline fragment with flexible alkoxy, fluoro and conjugated side chains.<sup>143</sup> It was shown that incorporation of the last has a positive impact not only on absorption spectra, but also on charge conductivity, energy levels and a microstructure of active layers in polymeric solar cells (PSCs) that leads to considerable improvement of productivity of photovoltaic devices.

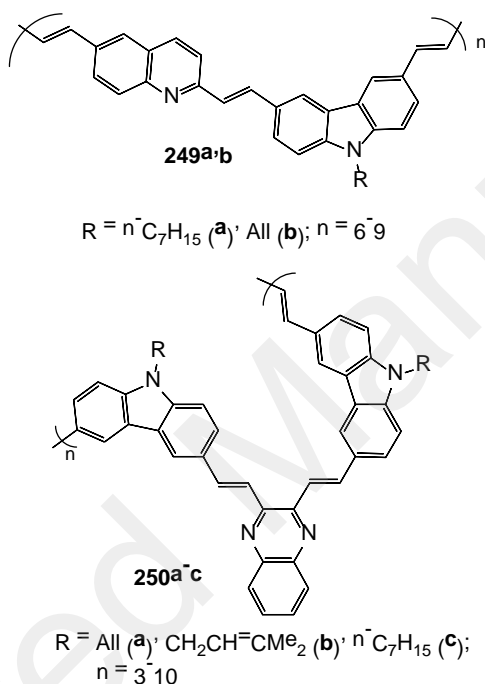
Liu and co-authors generalized data on quinoxaline-based D-A conjugated polymers, classifying them by the donor unit incorporated into the quinoxaline moiety.<sup>144</sup> Various replaced fluorenes, carbazoles, indacetodithiophenes, benzodithiophenes, thiophenes and other comonomers were considered as such donor unit. Modifications of chemical structure by two-dimensional side chains or fluorine substituents targeted to maximizing the productivity of solar cells were described.

Despite a large number and a variety of synthesized and studied  $\pi$ -conjugated polymers bearing acceptor quinoxaline fragments as well as some established "structure-properties" correlations, the search of new photoactive polymers with improved characteristics is continued.

Upadhyay and co-authors<sup>195,196</sup> synthesized novel series of donor-acceptor combined quinoline-carbazol oligomers **249**, using Wittig methodology. Compounds were characterized by

IR, NMR  $^1\text{H}$  and  $^{13}\text{C}$ , cyclic voltammetry, atom microscopy and TGA. Oligomers demonstrated thermostability up to 200 °C, good solubility in ordinary organic solvents. Oligomer **249a** possesses luminescence with  $\lambda_{\text{em}} = 420\text{--}451$  nm depending on the solvent polarity and  $\Phi_{\text{F}} = 0.23$  in chloroform. Oligomer **249b** also exhibited fluorescence with  $\lambda_{\text{em}} = 385\text{--}441$  nm in solution and 473 nm in film. The luminescence of these compounds can be quenched by the addition of dimethylaniline or dimethyl terephthalate to the solution of oligomer. Optical data allowed to conclude that strong intramolecular  $\pi\text{--}\pi^*$ -interaction between carbazole and quinoline takes place in oligomers.

### Structures 249, 250

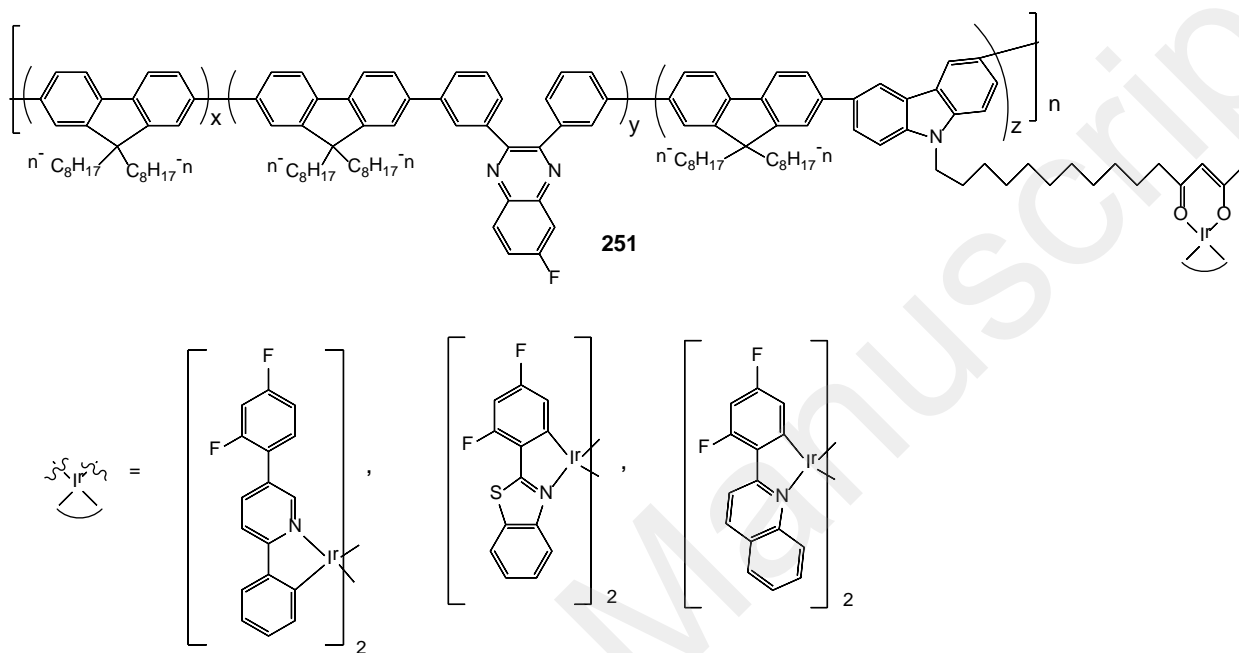


In another work the same authors<sup>197</sup> described synthesis and properties of oligomers **250a-c**, bearing quinoxaline cycle as an acceptor. Compounds are well soluble in organic solvents; decomposition temperatures exceeded 300 °C with 5% of weight loss. Oligomers exhibited fluorescence in solution, red shift of emission band is observed with increasing the solvent polarity. Thus, for compound **250a**:  $\lambda_{\text{em}} = 471$  (CHCl<sub>3</sub>), 521 nm (DMF),  $\Phi_{\text{F}} = 0.41$  (DMF); for **250b**:  $\lambda_{\text{em}} = 529$  nm,  $\Phi_{\text{F}} = 0.49$  (DMF); for **250c**:  $\lambda_{\text{em}} = 545$  nm,  $\Phi_{\text{F}} = 0.61$  (DMF). In solid state the emission peak underwent red shift up to 550, 562 and 574 nm for **250a-c** correspondently. As in the case of oligomer **249**, luminescence of compounds **250** can be quenched by the same quenchers. The behavior of oligomer **250** in relation to a wide range of metal cations was studied and it was shown that only the addition of a  $\text{Ni}^{2+}$  cation leads to strong decrease in fluorescence intensity. These compounds can be applied as selective probe on  $\text{Ni}^{2+}$  ions in the presence of other metals. According to authors, these oligomers have potential application in OLEDs.



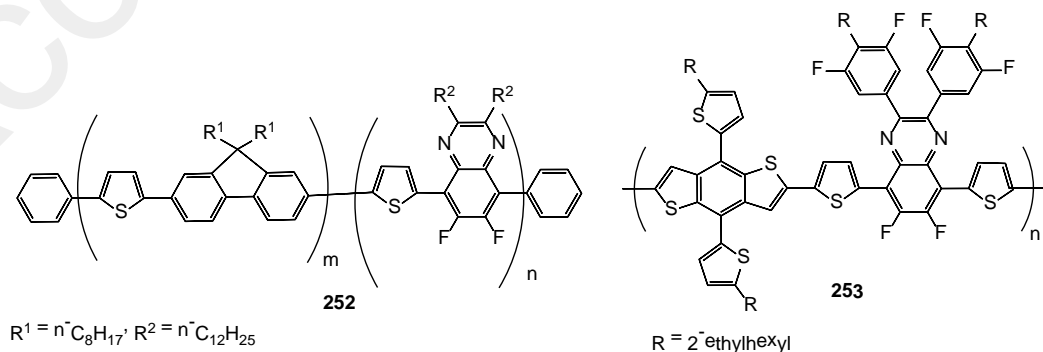
Guo and co-authors described white light emitting polymers **251** based on polyfluorene derivative, bearing electron-deficient 2,3-biphenyl-6-fluoroquinoxaline in the main chain, and imparted iridium complexes in side chain.<sup>198</sup> It is shown that the combination of blue fluorescence of the main chain and yellow phosphorescence of iridium complex resulted in effective white emission in this unique polymer.

Structure 251



In a number of works the improvement polymers properties was reached by the modification of quinoxaline fragment. Kang and co-authors<sup>199</sup> prepared five new co-polymers **252**, containing 2,3-dialkyl-6,7-difluoroquinoxaline and 9,9-dioctylfluorene with their different ratio in the main chain. All polymers demonstrated high  $M_w$ , good solubility in chlorine-containing solvents and high thermostability. These copolymers are characterized by rather low value of optical gap (1.93–2.08 eV) and deep level of HOMO energy (-5.67–-5.59 eV). PSCs based on co-polymers **252** were performed, these devices demonstrated maximum values of PCE in the range 2.91–3.98%.

Structures 252, 253

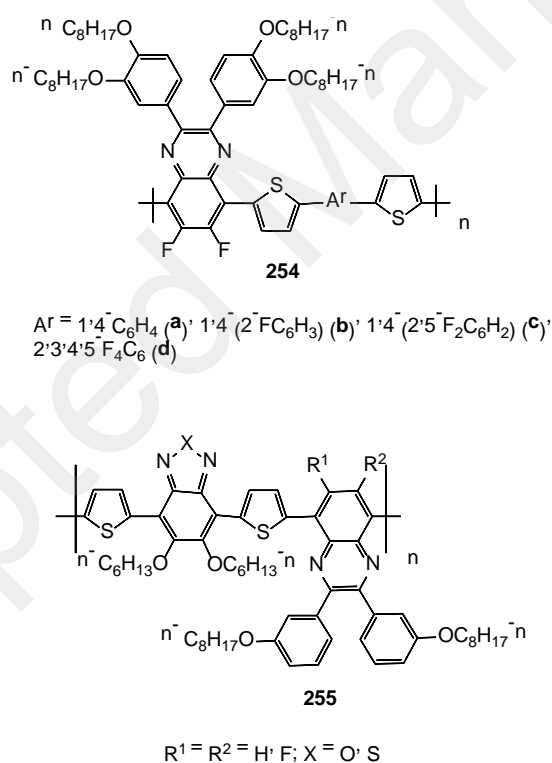


Wang and co-authors reported about novel  $\pi$ -conjugated co-polymer of D-A type **253**, including 4-alkyl-3,5-difluorophenyl-substituted quinoxaline as acceptor, disubstituted

benzodithiophene fragment as donor and thiophene as spacer in the main chain.<sup>200</sup> Organic solar cells (OSCs) based on **253** exhibited excellent efficiencies both in fullerene (PCE = 9.2%), and non-fullerene devices (PCE = 9.6%). Authors demonstrated that incorporation of two weak electron-donating groups into position 4 of phenyl substituent of quinoxaline led to the improvement of photovoltaic properties.

Yang and co-authors described new polymers **254** for effective non-fullerene OSCs, containing 3,4-dialkoxyphenyl-substituted quinoxaline and dithiophenearyl fragment.<sup>201</sup> It was shown that incorporation of 1–4 fluorine atoms into aryl fragment allows effective adjusting levels of polymer frontal molecular orbitals, molecular packing and the morphology of films. According to calculations, polymer **254c** is characterized by the greatest planarity due to intramolecular non-covalent S...F and H...F interactions. All polymers showed wide optical gap ( $E_g > 1.8$  eV) and the great value of switching voltage (1.00 V) in non-fullerene OSCs. The device based on polymer **254c** exhibited PCE = 9.7%.

#### Structures 254, 255

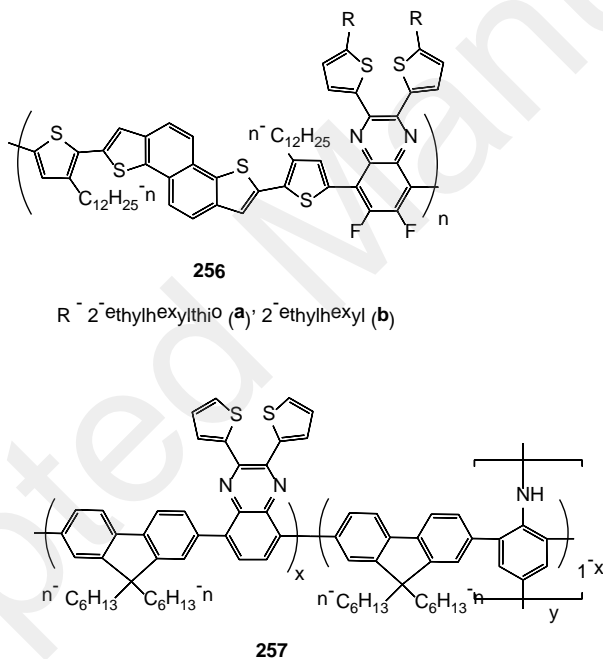


Wang and co-authors obtained triple co-polymers **255** of D-A<sub>1</sub>-D-A<sub>2</sub> structure by the combination of the simplest thiophene donor and two simple acceptors: alkoxy-containing benzoxadiazole (benzothiadiazole) and quinoxaline.<sup>202</sup> Studying of optical, electrochemical properties of these polymers, characteristics of the PSCs samples fabricated on the basis of **255** showed that variation of the structure of A<sub>2</sub> moiety allows adjustment of the specified properties of the final polymer. Copolymers absorbed in visible range with maximum at 565–630 nm in solution,

showed width of an optical gap within 1.70–1.73 eV and the deep level of HOMO energy (–5.60–5.34 eV). The maximum value of PCE = 5.84% was obtained for the device on the basis of copolymer **255** ( $X = O$ ,  $R^1 = H$ ,  $R^2 = F$ ), and it is much higher than for polymers of D-A<sub>1</sub> or D-A<sub>2</sub> type.

Lin and co-authors described new D-A polymers **256**, containing naphthodithiophene as donor and quinoxaline bearing alkylthio and alkylthiophene side chains.<sup>203</sup> Comparative studying of the influence of flexibility of such chains on polymers properties showed that alkylthio residues lead to the red shift of absorption bands, lowering of the HOMO and LUMO energy level, improvement of intermolecular  $\pi \cdots \pi$  interactions and the morphology of films. It was found that PSC based on polymer **256a** possessed higher value PCE (5.03 %), whereas for PSC using **256b** PCE was only 1.93%. Results of researches confirm an important role of substituents in quinoxaline acceptor on the tuning of properties of polymers and devices.

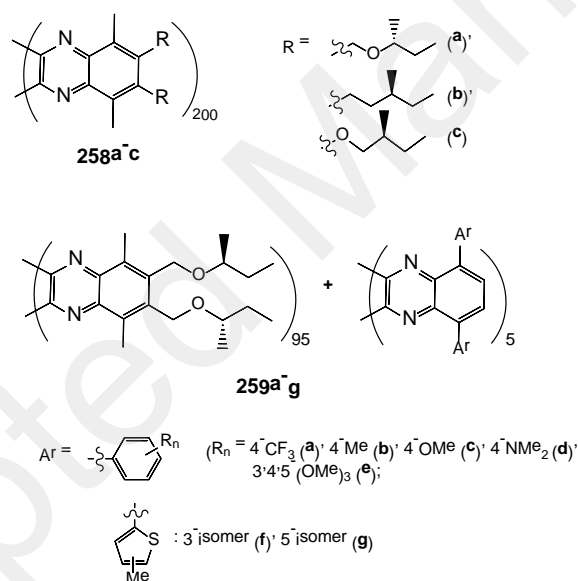
#### Structures 256, 257



In the work of Jessop and co-authors the two-dimensional conjugated polymer **257** based on aniline and 9,9-dihexylfluorene as donor fragments and 2,3-dithienylquinoxaline as acceptor was synthesized.<sup>204</sup> Comparison of the properties of this polymer with its one-dimensional precursor showed that the effect of perpendicular polyaniline branches resulted, mainly, in considerable reduction of molecular weight, whereas such characteristics as absorption and emission maxima, HOMO and LUMO energy level, size of optical gap practically do not change. OLED fabricated on the basis of polymer **257** as emissive layer, shows the low efficiency of the device, the electroluminescence arises at high value of switching voltage.

Nagata and co-authors synthesized and studied properties of polymers **258**, bearing quinoxalin-2,3-diyl with different chiral side chains.<sup>205</sup> These compounds were obtained by polymerisation of 1,2-diisocyano-4,5-R-benzenes in the presence of complexes of transitional metals, they possess spiral-like main chain caused by steric pushing of two substituents at positions 5 and 8 of quinoxaline.<sup>206</sup> Polymers **258** exhibited blue fluorescence in solution, the luminescence intensity for **258c** was much higher than for **258a,b**. The dependence of spiral inversion of polymers **258a-c** from the solvent was studied and it was shown that all of them possess *M*-spiral structure in  $\text{CHCl}_3$  and *P*-spiral in 1,1,1-trichloroethane (TCE). Spectra of a circular polarized luminescence (CPL) of polymer **258c** in the diluted solutions of several solvents, including  $\text{CHCl}_3$  and 1,1,1-TCE were registered, and it was shown that observed signals are obliged to spiral conformation of quinoxaline cycles. CD spectra in  $\text{CHCl}_3$  and 1,1,1-TCE were almost mirror display of each other. Thus, polymers demonstrated the chiral-switched CPL in the diluted solution and can be considered as the new class of CPL materials.

### Structures 258, 259

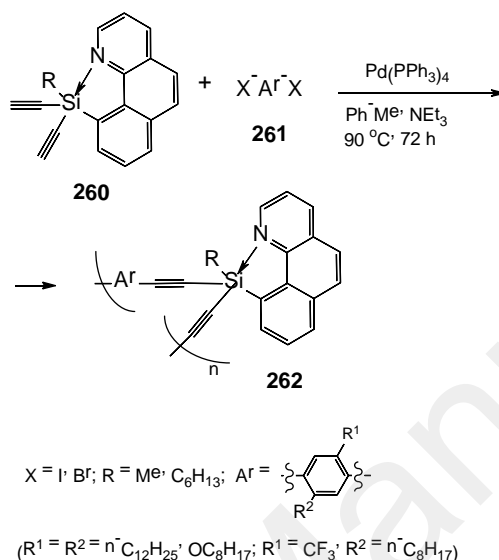


In another work the same group of authors<sup>207</sup> described co-polymers **259**, containing achiral luminescent 5,8-diarylquinoxalines and poly(quinoxalin-2,3-diyl) as main chain with chiral side chains in the ratio 95:5. These co-polymers possess multicolour emission; the colour depends on substituent Ar, red shift of  $\lambda_{\text{em}}$  was observed at the increase of electron donating ability of Ar. Thus, compounds **255a,b** exhibit blue emission, **259c,d** – green, **259e,f,g** – orange or red. Like polymers **258** co-polymers **259** possess *M*-spiral structure in  $\text{CHCl}_3$ . Copolymers **259** showed circular polarized luminescence and CPL spectra in 1,1,1-TCE were almost mirror display of the spectra recorded in  $\text{CHCl}_3$ , demonstrating that in 1,1,1-TCE they get *P*-spiral conformation. Having replaced (*S*)-2-butoxymethyl of side chain with (*S*)-3-octyloxymethyl one, authors obtained copolymers exhibiting significant correlation CPL from the nature of solvent (*n*-octane or

cyclooctane) while maintaining the wavelength of the CPL. These results showed that in such chiral co-polymers the luminophor and chiral component can be independent from each other. In this case poly(quinoxalin-2,3-diyl) is presented as a multifunctional chiral framework for CPL materials.

Tokoro and co-authors reported the synthesis and optical properties of conjugated polymers **262**, including penta-coordinated organosilicon complex based on benzo[*h*]quinoline.<sup>208</sup>

**Scheme 20**



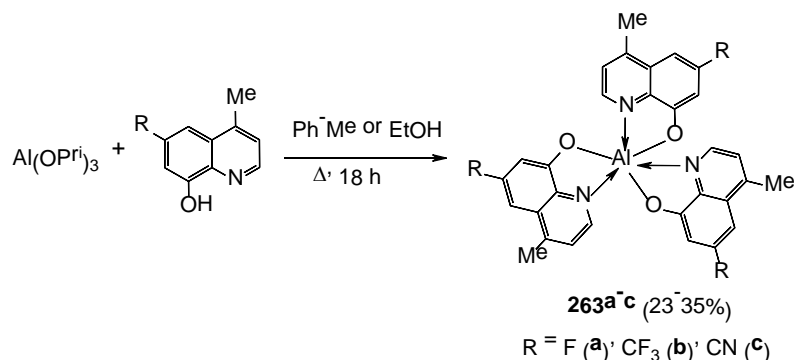
Compounds **262** were obtained from diethynyl monomers **260** and *n*-dihalogenated co-monomers **261** by cross-coupling Sonogashira-Hagihara reaction in 75–95% yield (Scheme 20). Polymers were characterized by NMR <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si and IR spectra data, possess good solubility in organic solvents. In THF these polymers possess intensive tunable luminescence with λ<sub>em</sub> = 417–474 nm depending on the nature of aryl substituent and quantum yield up to 0.24. This is the first example of the luminescent polymers containing pentacoordinate silicon.

## V. Coordination compounds of benzazines

Since the first data on the OLED based aluminum complex of 8-hydroxyquinoline (Alq<sub>3</sub>) possessing green fluorescence have been published,<sup>24</sup> this compound has been widely studied as an electron-transport and luminescent material. Numerous researches were also focused on optimization of Alq<sub>3</sub> structure for achievement of blue emission. Thus, authors of work<sup>209</sup> were synthesized derivatives **263** bearing electron-donor or electron acceptor groups at quinoline core in order to tune the value of HOMO-LUMO gap. Complexes **263** were obtained through the reaction of tri(isopropoxide)aluminium with 4-methyl-6-R-quinolines (Scheme 21), the structure of **263a** was confirmed by X-ray. In DCM solution complexes **263** exhibit blue fluorescence with λ<sub>max</sub> 478–482 nm and Φ<sub>F</sub> = 0.46–0.57, which exceeds the value for Alq<sub>3</sub> (Φ<sub>F</sub> = 0.15). Simple devices

using compounds **263** as an electron-transport and emitting material were created, the best value EQE (4.6%) was observed for OLED based on **263a**.

**Scheme 21**



Triplet energies of derivatives **263** were determined from the phosphorescence spectra recorded at 77K, these data also showed blue shift in comparison with Alq<sub>3</sub> and higher values in comparison with the Ir complexes on the basis of quinoline derivatives. Such characteristics allowed applying compounds **263** for the creation of OLEDs emitting white light (WOLEDs). The device based on the derivative **263a** showed EQE up to 19% and high purity of white light (color rendering index, CRI) ~ 80.<sup>209</sup>

Another approach for increasing the intensity of fluorescence of Alq<sub>3</sub> was developed.<sup>210</sup> Authors obtained organo-inorganic hybrid material in which Alq<sub>3</sub> chromophore is intercalated into zirconium phosphate modified with butylamine (BAZrP). This hybrid (Alq<sub>3</sub>/BAZrP) showed very intensive green-blue fluorescence with shift of  $\lambda_{em}$  up to 505 nm ( $\lambda_{em}$  = 515 nm for Alq<sub>3</sub>). Besides, the hybrid showed prolonged lifetime of the excited state that allows applying it in other areas, such as conversion and storage of solar energy.

In the last decades, many researches on coordination compounds of benzazines for optoelectronic materials have been directed to application of wide range of transitional elements, in which electronic structures d- and f-sublevels are filled. Transitional elements are divided into d-elements, lanthanides (4f-elements) and actinides (5f-elements), there are significant differences between these groups. d-Elements have a filling of nd-orbitals: 3d - 4d-, 5d- (three rows or three decades), d-elements of which differ in chemical properties from each other. Examples of 3d-metals are Mn, Fe, Co, Ni, Cu, Zn; 4d-metals include Ru, Pd, Ag, Cd; and 5d-metals are Os, Ir, Pt. Any d-orbitals in space leave far beyond the atom or an ion; therefore electrons on them are exposed to strong influence of a coordination environment. At the same time d-electrons strongly influence the next atoms and ions. Existence of incomplete configurations of d-orbitals of transitional metals atoms provides features of magnetic behavior of their compounds. The main feature of almost any d-element is the variable valency of its atoms.

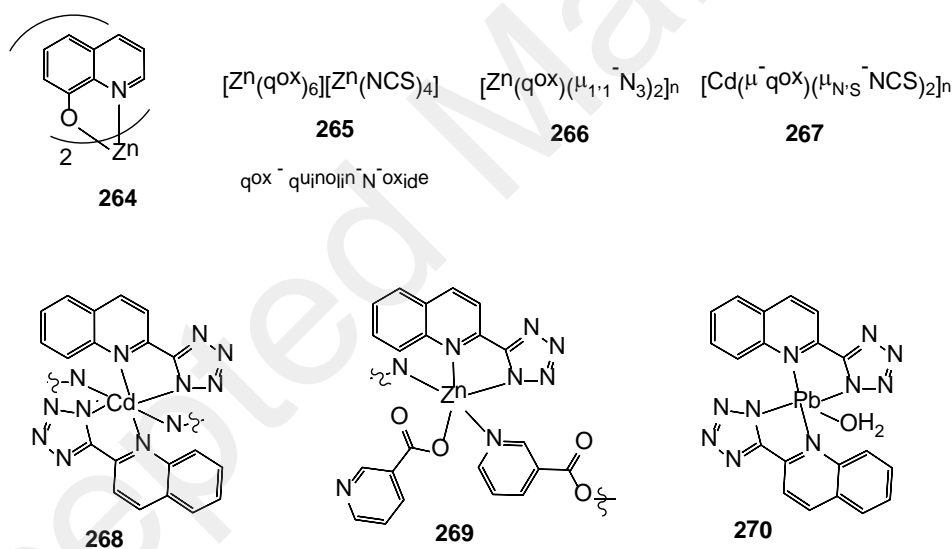
The review published by Katkova *et al*<sup>9</sup> is devoted to complexes of rare-earth elements with quinoline ligands, and a number of Os, Ir, Pt complexes with azine ligands are presented.<sup>8,211</sup>

## V.1. Complexes of benzazines with d-metals

### V.1.1. Complexes with Zn<sup>II</sup>, Cd<sup>II</sup>, Co<sup>II</sup>, Cu<sup>I</sup>, Ag<sup>I</sup>, Pd<sup>II</sup>

Quinoline derivatives containing coordinating group at positions 8 or 2 remain the most promising ligands for obtaining complexes with luminescent properties. Photophysical, thermal and electronic properties of polyaniline (PA) composite with zinc bis(8-hydroxyquinolate) **264**, obtained by oxidative polymerization, are compared with properties of free Zn complex.<sup>212</sup> It is shown that doping of PA with zinc complex led to the increase in thermostability and conductivity. The intensity of fluorescence of composite increased considerably, and it can show purple emission with  $\lambda_{em} = 423$  nm under excitation at  $\lambda_{exc} = 340$  nm, or blue emission with  $\lambda_{em} = 468$  nm under excitation at  $\lambda_{exc} = 360$  nm. This polymeric composite represents potential material for electronic and optoelectronic application.

#### Structures 264-270

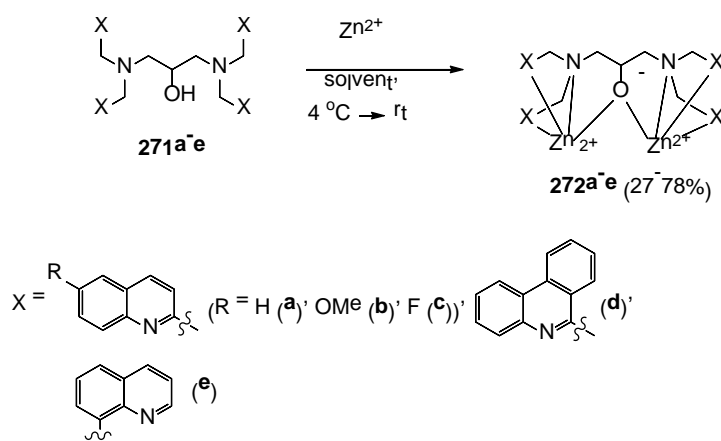


Quinoline-N-oxide (qox) was used as O-ligand for the synthesis of Zn<sup>II</sup> and Cd<sup>II</sup> complexes **265-267**.<sup>213</sup> The structures of these compounds were determined by X-ray method. Complex **265** consists of octahedral cation  $[Zn(qox)_6]^{2+}$  and tetrahedral anion  $[Zn(NCS)_4]^{2-}$ . In complex **266** the Zn<sup>II</sup> centers with coordination number 5 are connected with azide groups in a polymeric chain. Octahedral Cd<sup>II</sup> centers in complex **267** are connected in a polymeric chain with ligand molecules and isothiocyanate-anions. In solid state, Zn complexes **265** and **266** exhibit luminescence with broad emission band, aligned at 621 and 614 nm respectively, whereas complex **267** shows two emission maxima – at 618 and 654 nm.

Complexes  $\text{Cd}^{\text{II}}$  (**268**),  $\text{Zn}^{\text{II}}$  (**269**) and  $\text{Pb}^{\text{II}}$  (**270**), synthesized by solvothermal reaction of quinoline-2-carbonitrile, sodium azide and metal chloride in the presence of  $\text{NH}_4\text{Cl}$  (for **268**) or nicotinic acid (for **269**), were presented.<sup>214</sup> According to X-ray data, complex **268** represents linear polymer in which Cd ion has an octahedral environment formed by six nitrogen atoms of four quinoline-tetrazole ligands. Zinc atom in complex **269** also surrounded in octahedral way with four nitrogen atoms and two oxygen atoms of nicotinic acid. In compound **270**, the square-pyramidal environment of Pb ion takes place. All complexes possess strong luminescence in solid state. Compound **268** exhibited blue emission with  $\lambda_{\text{em}} = 494$  nm, the spectrum of complex **269** contains two bands with maximum at 464 nm and 580 nm, in both cases emission is short-lived (10-12 nsec). Unlike them the Pb complex **270** showed yellow emission with  $\lambda_{\text{em}} = 550$  nm and longer lifetime (125  $\mu\text{sec}$ ).

Binuclear  $\text{Zn}^{\text{II}}$  complexes (**272**) were obtained on the basis of tetrakis-quinoline ligands **271** (Scheme 22), compounds **272** were investigated for fluorescent sounding of phosphate anions.<sup>215</sup> The formation of complexes **272** with composition ligand: $\text{Zn}^{2+} = (1:2)$  in solutions was controlled by monitoring of changes in absorption and fluorescence spectra under addition of  $\text{Zn}^{2+}$  ions to a ligand. The composition and structure of complexes  $[(\mathbf{272c-e})(\text{AcO}^-)(\text{ClO}_4^-)_2]$ , obtained from ligands **271c,d,e** and acetate or perchlorate, were confirmed by X-ray method. Each zinc ion in these complexes is pentacoordinated with three nitrogen atoms, one oxygen atom from a ligand and another oxygen atom from acetateanion. Complexes **272a,c,e** demonstrated weak fluorescence with  $\lambda_{\text{em}} = 450$  nm, addition of pyrophosphate (PPi) up to 1 equiv. led to the increase of intensity, and further addition of PPi resulted in the decrease. Such changes are due to the formation of triple complex ligand- $\text{Zn}^{2+}$ -PPi (1:2:1) corresponding to the emission maximum, and then removal of Zn under the excess of pyrophosphate takes place.  $\text{Zn}_2$ -Complex **272a** showed the best results in experiments with pyrophosphates and was used for determination of enzymatic activity of pyrophosphatase.

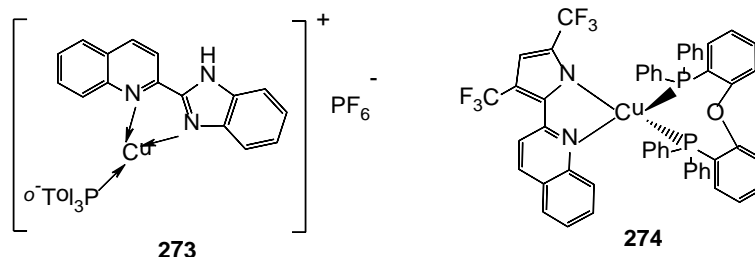
Scheme 22





Complex **273**, obtained on the basis of 2-(benzimidazol-2-yl)quinoline and tri(*o*-tolyl)phosphine also contains tricoordinated Cu<sup>I</sup> atom, according to X-ray data.<sup>216</sup> Compound **273** possesses strong yellow phosphorescence proved to be perspective for OLED.

#### Structures 273, 274



Neutral complex Cu<sup>I</sup>**274** was synthesized using 3,5-bis(trifluoromethyl)-2-(quinolin-2-yl)pyrrole as *N,N*-ligand and bidentate phosphine auxiliary ligand.<sup>217</sup> In DCM solution at room temperature compound **274** possesses orange-red luminescence with  $\lambda_{em} = 603$  nm and  $\Phi_F = 0.12$ . In a firm matrix (77K) the blue shift of a maximum of emission  $> 50$  nm and the increase in  $\Phi_F$  up to 51% (total on fluorescence and phosphorescence bands) take place, thus, the complex shows rigidochromism.

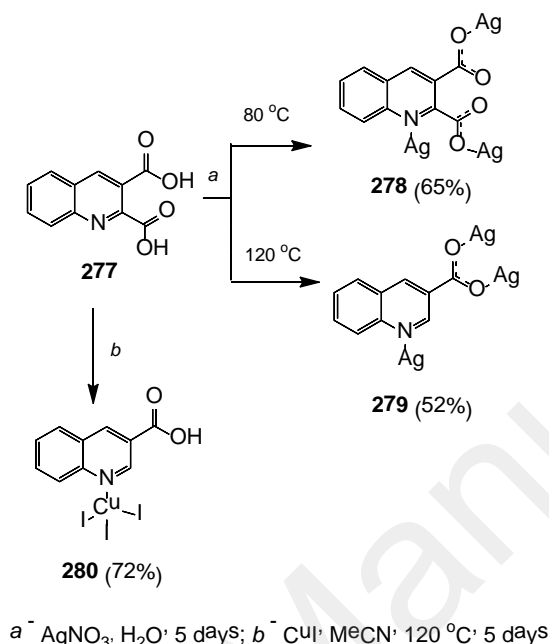
The design of coordination polymers drew special attention due to their some interesting physical and optical properties and the possibility of use as multifunctional materials. Polymeric Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> complexes with general formula  $[M(dca)_2(quin)_2]_n$  (**275a-c**) were obtained by the reaction of quinoxaline (quin), metal acetate and subsequent addition of dicyanamide (dca) in the ratio 1:1:2 in methanol.<sup>218</sup> According to X-ray data, complexes are isostructural and represent 1D coordination polymers. Complexes exhibit strong blue fluorescence both in methanol and solid state ( $\lambda_{em} = 407\text{--}445$  nm,  $\Phi_F = 0.21\text{--}0.70$ ). Zinc complex **275a** possesses the highest intensity with  $\Phi_F = 0.70$ , possibly, because of stronger  $\pi \dots \pi$  interactions between quinoxaline fragments.

Mixed Cd<sup>II</sup> complexes on the basis of quinazoline (qnz) and second co-ligand with compositions  $[Cd(qnz)_2(SCN)_2]_n$  (**276a**),  $[Cd(qnz)_2(dca)_2]_n$  (**276b**),  $[Cd(qnz)_2(N_3)_2]_n$  (**276c**) were synthesized and characterized in work.<sup>219</sup> Polymeric structures of compounds **276a,b** were confirmed by X-ray method. All three complexes exhibit strong fluorescence in solid state with  $\lambda_{em} = 397$  nm and the type of spectra is close to a spectrum of initial quinazoline ligand.

Coordination Cu<sup>I</sup>, Ag<sup>I</sup> polymers with some azine ligands exhibit interesting luminescent properties and already find application for obtaining the emitting layers in polymeric LED.<sup>220</sup> Complexes of Ag<sup>I</sup> (**278**, **279**) and Cu<sup>I</sup> (**280**), synthesized on the basis of 2,3-quinolinedicarboxylic acid (H<sub>2</sub>qldc) (**277**) in the conditions of hydrothermal reaction, were presented.<sup>221</sup> It is established that temperature has an impact on the structure of final product (Scheme 23). Thus, at 80 °C complex **278** with preservation of both carboxyl groups is formed, and at 120 °C decarboxylation

takes place, and complexes of both silver, and copper (**279**, **280**) are formed on the basis of 3-quinolinecarboxylic acid (3-Hqlc). According to X-ray data, in structures **278**, **279** silver atom is coordinated with one nitrogen atom and two oxygen atoms from other quinoline molecules; copper atom in the structure **280** is coordinated with three iodine atoms and one nitrogen atom.

Scheme 23



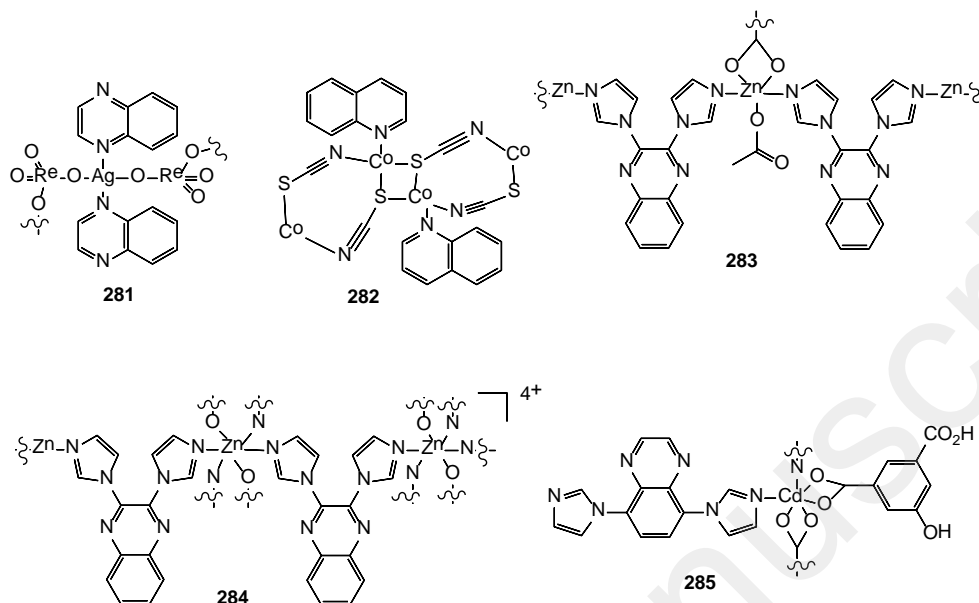
Both  $\text{Ag}^{\text{I}}$  complexes exhibit stable blue luminescence in solid state and solution with intensive emission band at 404–427 nm depending on solvent nature at 298 K, at 77 K red shift of emission band was observed.  $\text{Cu}^{\text{I}}$  complex demonstrates tunable luminescence at 298 K and 77 K from yellow to red, demonstrating thermochromic behavior. Polymethyl methacrylate doped by complex **280** shows higher intensity of yellow luminescence, improved thermostability and longer lifetime of the excited state than initial coordination polymer **280**.<sup>221</sup>

Coordination polymer based on  $\text{Ag}^{\text{I}}$  with composition  $[\text{Ag}(\text{quin})](\text{ReO}_4)$  (**281**) was obtained by reaction of  $\text{AgReO}_4$  with quinoxaline (quin) in acetonitrile at room temperature.<sup>222</sup> According to X-ray data, structure **281** includes cationic polymer chains built from  $[\text{Ag}(\text{quin})]^+$ , in which silver ion possesses almost linear geometry. Two oxygen atoms of anion  $(\text{ReO}_4)^-$  act as bidentate bridges, connecting chains in 3D supramolecular structure. The obtained complex showed luminescence with emission bands at ~ 615 nm, 550 nm (as in initial quinoxaline) and an additional band at 445 nm.

New one-dimensional coordination polymer based on  $\text{Co}^{\text{I}}$  with composition  $[\text{Co}(\text{SCN})(\text{gl})]_n$  (**282**) was synthesized by reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with KSCN with quinoline (gl) in the mixture water/MeCN at room temperature.<sup>223</sup> According to X-ray data,  $\text{Co}^{\text{I}}$  atom possesses distorted trigonal-pyramidal environment  $\text{N}_2\text{S}_2$  with two S atoms and one N atom from the third thiocyanate

anion as well as N atom from quinoline ligand. Polymer shows blue luminescence with  $\lambda_{\text{em}} = 415$  and 435 nm in solid state at ambient temperature.

### Structures 281-285

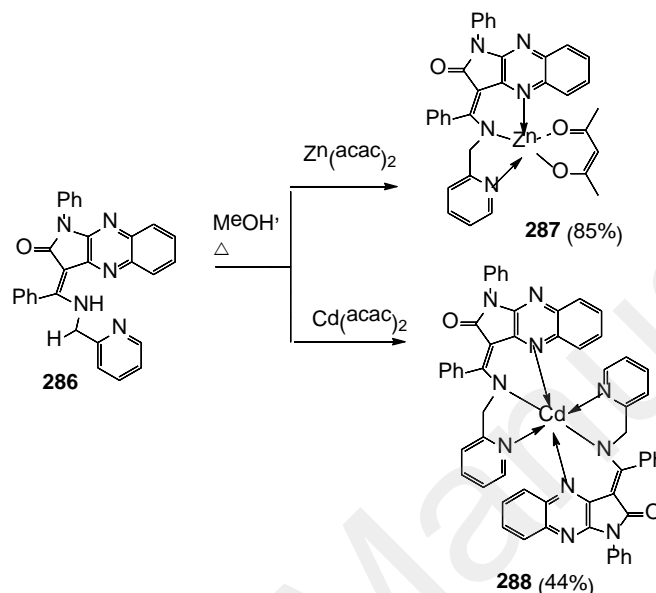


Quinoxaline derivatives including annelated ones also often act as ligands for metal complexes. Thus reaction of 2,3-bis(imidazol-1-yl)quinoxaline (biimquin) with zinc acetate led to polymeric complex  $[\text{Zn}(\mu_2\text{-biimquin})(\text{OAc})_2] \cdot \text{H}_2\text{O}$  (**283**), whereas in the case of zinc chloride  $[\text{Zn}(\mu_2\text{-biimquin})_2(\text{H}_2\text{O})_2] \cdot 4\text{Cl} \cdot \text{H}_2\text{O}$  (**284**) was formed.<sup>224</sup> Composition and structure of complexes were determined by X-ray method. In a one-dimensional zigzag chain of complex **283**  $\text{Zn}^{\text{II}}$  atoms are connected with ligands by the bridge through imidazole nitrogen atoms. In the complex **284** ligands are connected in the same way, but the structure is presented by a one-dimensional sphere-like double chain. Both complexes in solid state at room temperature show an intensive blue luminescence with  $\lambda_{\text{em}} = 387$  nm (**283**) and 426 nm (**284**).

$\text{Cd}^{\text{II}}$  complex on the basis of 5,8-di(1*H*-imidazol-1-yl)quinoxaline (biimquix) (**285**) was obtained by solvothermal reaction, and ligand was formed *in situ* from 3,6-di(4*H*-imidazol-4-yl)benzene-1,2-diamine and glyoxal.<sup>225</sup> According to X-ray data, the composition of **285** is  $\{[\text{Cd}(\text{biimquix})(\text{hip})] \cdot 2\text{H}_2\text{O}\}_n$ , where hip is deprotonated 5-hydroxyisophthalic acid. Each  $\text{Cd}^{\text{II}}$  center is hexacoordinated with two nitrogen atoms from different biimquix ligands and with four carboxylate oxygene atoms from two different hip. In solid state at room temperature complex exhibited intense wide emission band at  $\lambda_{\text{em}} = 454$  nm. The sensitivity of this complex towards different metal ions was studied and it was shown that under addition of  $\text{Fe}(\text{NO}_3)_3$  solution in DMF the intensity of emission of complex is quenched by 82.5%, what considerably surpasses the sensitivity to other ions. It allowed recommending the complex **285** for luminescent detecting of  $\text{Fe}^{3+}$ .

New (*N,N,N*)-tridentate ligand **286**, bearing 2-aminomethylpyridyl group at enaminopyrrolo[2,3-*b*]quinoxalin-2-one, formed complex **287** under reaction with  $\text{Zn}^{\text{II}}$  acetylacetonate and complex **288** under the treatment with  $\text{Cd}(\text{acac})_2$  (Scheme 24).<sup>226</sup> Structure and composition of complexes were determined by X-ray method. Both complexes in solid state exhibit green luminescence with emission maximum at 472 nm (**287**) and 473 nm (**288**).

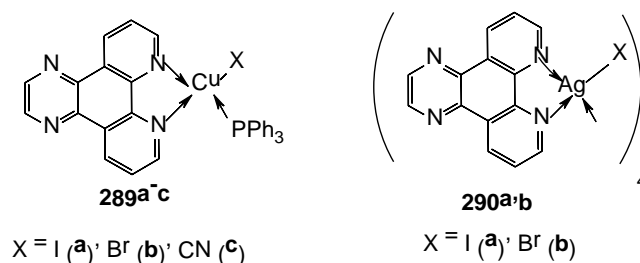
Scheme 24



$\text{Cu}^{\text{I}}$  complexes **289a,b** were synthesized on the basis of dipyrrolo[3,2-*f*:2,3-*h*]quinoxaline (dpquin) and triphenylphosphine.<sup>227</sup> According to X-ray data, complexes are polynuclear and isostructural; and in crystals favorable paired  $\pi \dots \pi$ -stacking takes place. These complexes possess an intensive luminescence in ethanol solution at room temperature with  $\lambda_{\text{em}}$  at 451, 470 nm, the observed red shift relative to dpq ( $\lambda_{\text{em}} = 419$  nm) is caused by the coordination of ligand with copper atom.

CN-substituted complex **289c** in DMF solution demonstrates blue luminescence with  $\lambda_{\text{em}} = 417$  nm, hypsochromic shift relative to ligand's emission band ( $\lambda_{\text{em}} = 430$  nm) takes place.<sup>228</sup>

Structures 289, 290



Complexes of  $\text{Ag}^{\text{I}}$  **290a,b** with composition  $[\text{AgX}(\text{dpquin})]_4$ , were obtained by slow diffusion method for the first time.<sup>229</sup> According to X-ray data, **290a,b** are isostructural and tetranuclear. Structure **290a** includes four symmetrically equivalent cations  $[\text{Ag}(\text{dpquin})]^+$

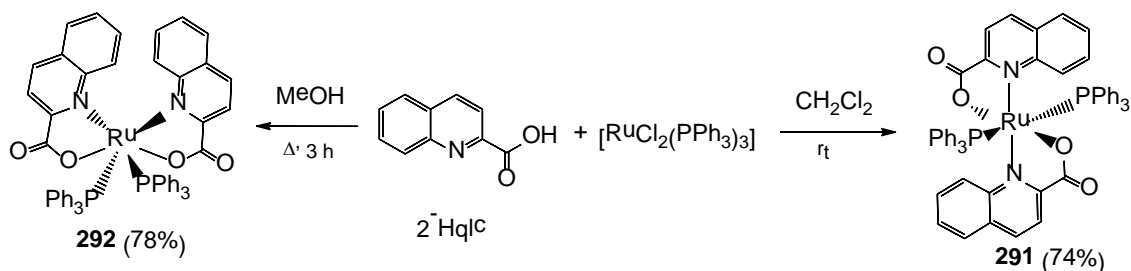
connected in a square with four  $\mu$ -bridged iodine anions. Ag atom is in tetrahedral environment formed by two nitrogen atoms of dpq and two I. In crystals of **290a,b** complexes  $\pi\cdots\pi$ -stacking interaction and Ag-Ag interaction take place. Both complexes possess an intensive photoluminescence in ethanol solution at room temperature with emission maxima at 450, 470 and 480 nm.

Ability of numerous benzazine derivatives to coordinate easily with metal ions is often used for their studying as sensors on metal ions. So, in work<sup>230</sup> the Schiff base obtained from 8-aminoquinoline and 2-imidazolcarboxaldehyde was investigated as the selective and reversible luminescent hemosensor for  $\text{Zn}^{2+}$  ions in the mixture water/methanol with a limit of detection  $5.81 \times 10^{-6}$  M. Another Schiff base synthesized from 1-aminopyrene and 8-hydroxyquinoline-2-carboxaldehyde proved to be selective reversible luminescent chemosensor for  $\text{Fe}^{3+}$  ions in aqueous medium with a limit of detection  $2.52 \times 10^{-8}$  M.<sup>231</sup>

### V.1.2. Complexes with $\text{Ru}^{\text{II}}$

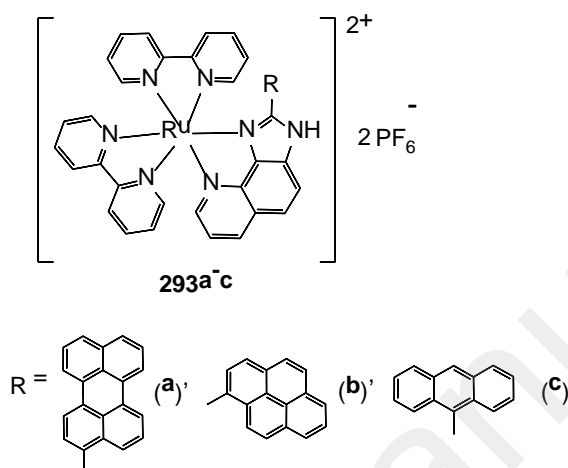
Among the transitional metals  $\text{Ru}^{\text{II}}$  drew close attention in coordination chemistry due to its stability, structural novelty and a number of interesting photophysical and photochemical properties, including ability to adjust color scale of luminescence in a wide spectral interval. Complexes of  $\text{Ru}^{\text{II}}$  represent one of the most studied classes of phosphorescent materials as they often emit in red region, though with a small quantum yield, such as complexes of  $\text{Ru}^{\text{II}}$  with azine ligands.<sup>232</sup>  $\text{Ru}^{\text{II}}$  complexes of general formula *cis/trans*- $[\text{Ru}(\text{PPh}_3)_2(2\text{-Hqlc})_2]$  (**291**, **292**) with 2-quinolinarboxylic acid (2-Hqlc) as co-ligand (Scheme 25) were synthesized and studied.<sup>233</sup> *trans*-Isomer **291** was obtained in DCM at room temperature, whereas *cis*-isomer **292** – under reflux in methanol. The structure of complexes was confirmed by X-ray method, the ruthenium atom geometry in both isomers represents the distorted octahedron. Interesting that *cis*-isomer **292** exhibited strong luminescence in DCM with  $\lambda_{\text{em}} = 324$  nm and low-intensive emission in methanol ( $\lambda_{\text{em}} = 343$  nm) under irradiation at  $\lambda = 281$  nm, at the same time *trans*-isomer **291** is non-emissive. For these complexes the property is defined by both metal environment geometry, and polarity of solvent.

Scheme 25



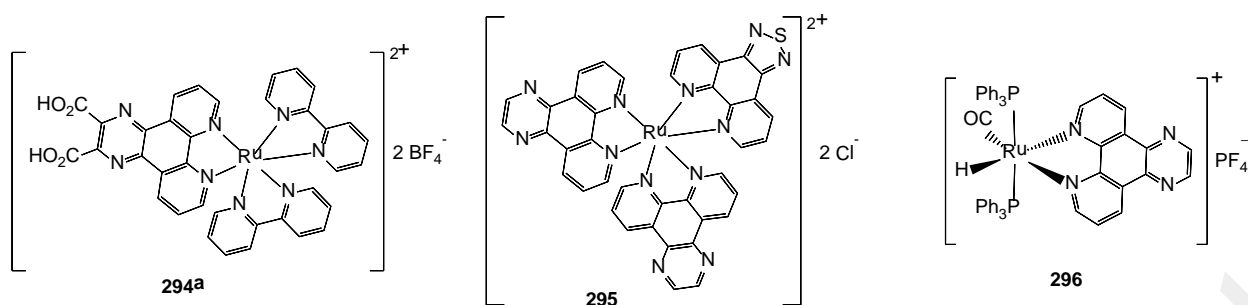
Three novel Ru<sup>II</sup> complexes **293a-c** with expanded  $\pi$ -conjugated system in the second ligand (imidazoquinoline) were obtained and studied by spectral methods.<sup>234</sup> Solutions of complexes in DMF demonstrate red or orange luminescence with emission maxima at 621 nm (**293a**), 607 nm (**293b**) and 603 nm (**293c**). Authors demonstrated that substitution of anthracene with pyrene or perylene in auxiliary ligand allows tuning the quantum yield and lifetime of emission.

#### Structures 293a-c



Ru<sup>II</sup> complexes with dipyrido[3,2-*f*:2,3-*h*]quinoxaline (dpq) derivatives as main ligand were described.<sup>174,175</sup> Thus, complexes with composition  $\{\text{Ru}[\text{dpquin}(\text{COOH})_2]_x(\text{L})_{3-x}\}^{2+}$  (**294**), where  $\text{dpquin}(\text{COOH})_2$  is 6,7-dicarboxydipyrido[3,2-*f*:2,3-*h*]quinoxaline, L = bpy or phen, were synthesized.<sup>174</sup> 6,7-Dicyanoderivative dpquin was used as starting compound, its refluxing with  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$  in the ratio 1:1 in acetonitrile and subsequent addition of  $\text{NaBF}_4$  led to the formation of complex  $\{\text{Ru}[\text{dpquin}(\text{COOH})_2](\text{bpy})_2\}(\text{BF}_4)_2$  (**294a**). Varying conditions, type of an auxiliary ligand and a ratio of ligands, authors obtained complexes with composition  $\{\text{Ru}[\text{dpquin}(\text{COOH})_2]_2(\text{bpy})\}(\text{BF}_4)_2$  (**294b**),  $\{\text{Ru}[\text{dpquin}(\text{COOH})_2](\text{phen})_2\}(\text{BF}_4)_2$  (**294c**),  $\{\text{Ru}[\text{dpquin}(\text{COOH})_2]_2(\text{phen})\}(\text{BF}_4)_2$  (**294d**),  $\{\text{Ru}[\text{dpquin}(\text{COOH})_2]_3\}(\text{BF}_4)_2$  (**294e**). All compounds **294** exhibit luminescent properties with red shift of emission maximum in acetonitrile from 513 nm (**294a**) to 646 nm (**294e**). LEDs created on the basis of these complexes demonstrated a possibility of tuning of electroluminescence color from blue-green to orange through the close to white ( $\lambda_{\text{em}}$  changed from 485 nm (**294a**) up to 572 nm (**294e**)). The best characteristics were shown by the device on the basis of complex **294a**.

#### Structures 294-296



Ru<sup>II</sup> complex **295**, containing two dpquin ligands and [1,2,5]-thiadiazolo-[3,4-f][1,10]-phenantroline as auxiliary ligand, was presented.<sup>175</sup> Compound exhibits intensive red luminescence with wide emission band with maximum at 637 nm (in DMF and water).

The new family of the luminophores based on Ru<sup>II</sup> complexes is represented by compound **296** in which only one diimine ligand (dpquin) and four different auxiliary ligands are present.<sup>176</sup> Complex was synthesized by ligand-substitution reaction of precursor [Ru(CO)(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with dpquin in ethanol under reflux. The structure **296** was confirmed by X-ray method. This complex exhibits orange luminescence with emission maximum at 592 nm in DCM at room temperature. In the vitrified environment at 77 K, blue shifted emission ( $\lambda_{em}$  up to 531 nm) and increase in excited state lifetime from 2.16  $\mu$ s (in solution) up to 188.3  $\mu$ s take place. Comparison of characteristics of complex **296** with other compounds of this group allows authors to conclude that the strengthening in a rigidity and  $\pi$ -conjugation in diimine ligand leads to the increase in luminescence effectiveness.

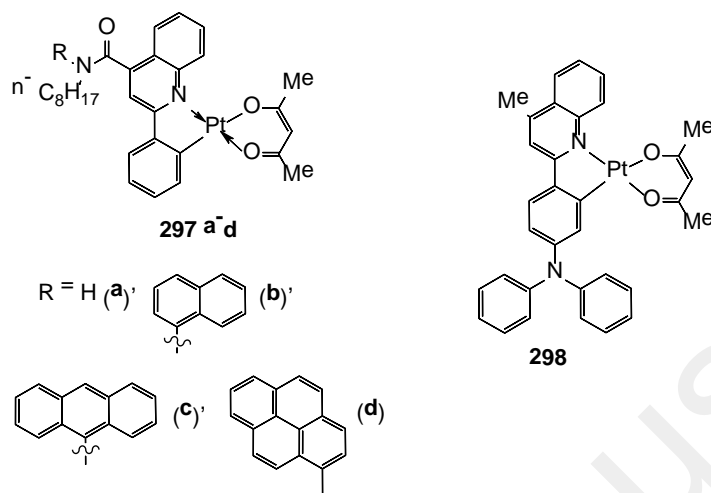
### V.1.3. Complexes with Pt<sup>II</sup>

Cyclometallated Pt<sup>II</sup> complexes represent compounds containing five-membered metallocycle with covalent C-Pt bond. Such complexes attracted considerable interest in the last decades and already found various applications due to tunability of their photophysical properties and possibility to apply of both singlet and triplet excitons for the increase of electroluminescence effectiveness.<sup>209</sup> Complexes of such type are mixed liganded, and along with a bidentate cyclometallating (C<sup>^</sup>N) ligand N,O-, N,S-, O,O-, N,X- and other bi- and monodentate ligands are used as co-ligands.

For tuning the emission of platinum complexes the introduction of chromophore groups in the structure of (C<sup>^</sup>N) ligand or changing the nature of co-ligand are used. The functionalized complexes **297**, containing *N*-octylcarboxamide residue with chromophore group R in quinoline fragment and acetylacetonate (acac) as co-ligand, were synthesized.<sup>235</sup> The structure of compounds **297c,d** was confirmed by X-ray data. Studying of luminescence of these complexes in aerobic and degassed solutions at ambient temperature and at 77K showed that chromophore-containing compounds **297b-d** exhibit double emission: fluorescence due to chromophore with  $\lambda_{em}$  < 500 nm

and phosphorescence with  $\lambda_{\text{em}} \sim 605$  nm. In case of a pyrenyl derivative **297d**, sharp increase in emission lifetime  $^3\text{MLCT}$  (up to 42  $\mu\text{s}$ ) was noticed, that could be due to a proximity of energies  $^3\text{MLCT}$  and  $^3\text{LC}$  in excited states and a possibility of energy transmission process between them.

### Structures 297, 298

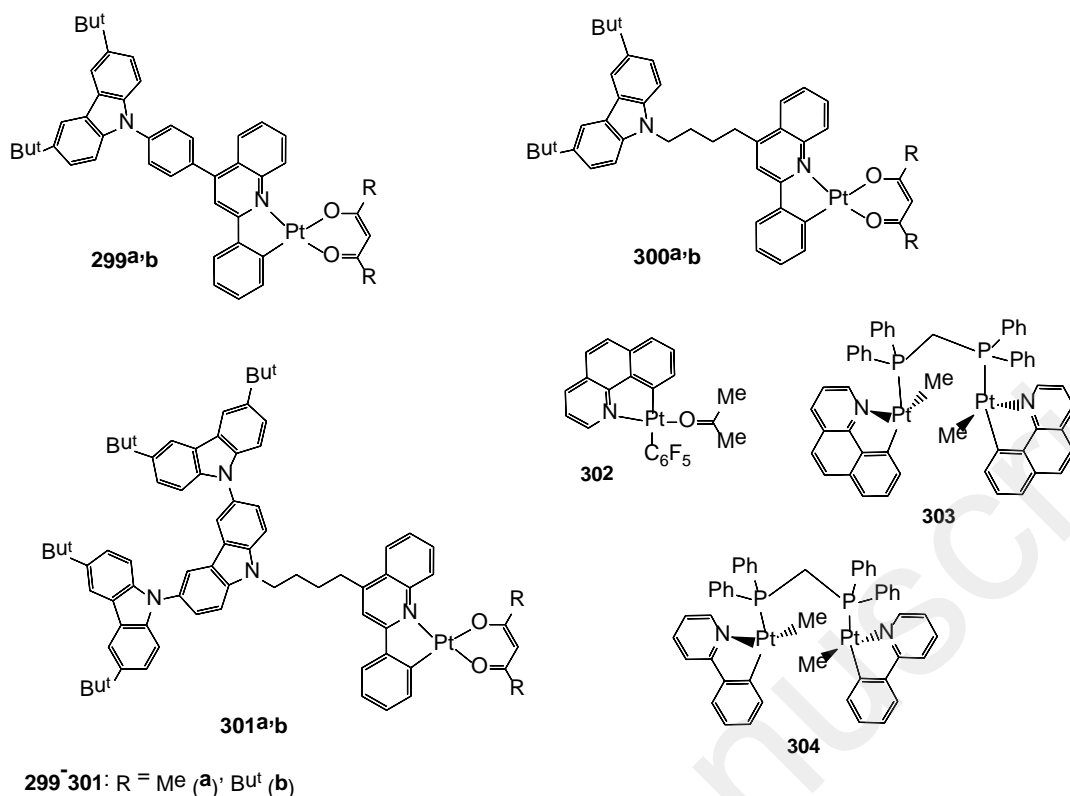


On the basis of quinoline ( $\text{C}^{\wedge}\text{N}$ ) ligand, bearing a strong electron donating substituent such as triphenylamine and acac as co-ligand, cyclometallated complex **298** was obtained.<sup>211</sup> Compound **298** demonstrated red phosphorescence with  $\lambda_{\text{em}} = 593$  nm and high quantum yield (0.99), it was used as a dopant for the creation of highly effective OLED.

New  $\text{Pt}^{\text{II}}$  complexes of dendrimer structure **299-301**, in which emitting base (ppq)Pt(acac/dmp) (ppq is 2,4-diphenylquinoline, acac is acetylacetone and dmp is dipivaloylmethane) and carbazole dendron are connected with flexible *n*-butylene chain (**300**, **301**) or rigid *n*-phenylene bridge (**299**) were synthesized.<sup>236</sup> All compounds were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and mass-spectrometry analysis, and the structures of complexes **299b**, **301a** were confirmed by X-ray method. The influence of dendrons and the linker on photophysical properties and the packing of complexes were studied. The intensive bands in absorption spectra at 409–415 nm corresponding to  $d\pi(\text{Pt})-\pi^*(\text{L})$  metal-ligand charge transfer (MLCT) mixed with the triplet LC transition were noted. All complexes exhibit bright red phosphorescence in DCM at room temperature with  $\lambda_{\text{em}} \sim 608$  nm. In films, emission spectra are widened and shifted to the long-wave range. It is shown that flexible *N*-butylene linker practically does not affect photoluminescent properties, but change the molecular packing that leads to the emergence of material guest function. Compounds **299-301** possess also electroluminescence, OLED devices were created on the basis of them, and the device based on the complex **301a** demonstrated the best characteristics.

### Structures 299-304





In some works<sup>171,172,237</sup> benzo[*h*]quinoline was used as (C<sup>^</sup>N) ligand for the synthesis of cyclometallated Pt<sup>II</sup> complexes **302**, **303**.

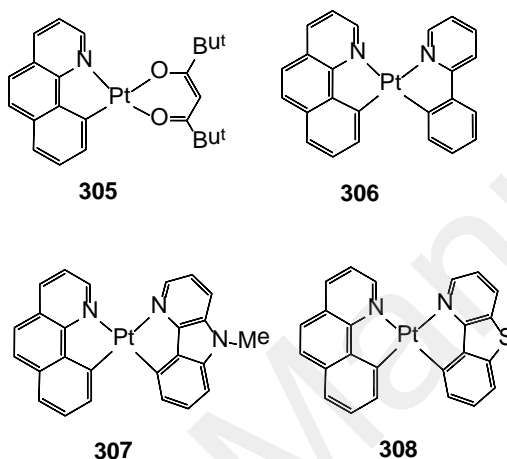
Complex Pt<sup>II</sup> with benzo[*h*]quinoline (bzql) (**302**) was synthesized by the reaction of activating precursor [*cis*-Pt(Ph)<sub>2</sub>(thf)<sub>2</sub>] with benzoquinoline in boiling acetone during 2.5 h.<sup>171</sup> This compound was characterized with only spectral data. Interaction of complex **302** with equimolar amount of terminal alkynes or diphenylacetylene led to the formation of the corresponding  $\eta^2$ -alkyn-containing complexes [Pt(bzql)(C<sub>6</sub>F<sub>5</sub>)( $\eta^2$ -HC≡CR)] (R = Ph, Bu<sup>t</sup>, ferrocenyl) or [Pt(bzql)(C<sub>6</sub>F<sub>5</sub>)( $\eta^2$ -PhC≡CPh)]. Complex **302** exhibit luminescence in solid state and solution at room temperature and 77K, arising mainly from intraligand (bzql) excited state with some mixing with <sup>3</sup>MLCT. In emission spectra bands at 477–482 nm and 553–595 nm are observed, their ratio depends on excitation wavelength, temperature and aggregate state. It should be noted that this complex demonstrates the considerable luminescent thermochromism (green at 77 K, orange at 298 K). The alkyne-containing complexes obtained from **302** also possess luminescent properties.

Binuclear cyclometallated complexes of methylplatinum(II), containing benzo[*h*]quinoline (**303**) or 2-phenylpyridine (**304**) as (C<sup>^</sup>N) ligand, were described.<sup>237</sup> Compounds were obtained by the substitution of SMe<sub>2</sub> co-ligands in the complex [PtMe(SMe<sub>2</sub>)(C<sup>^</sup>N)] with bis(diphenylphosphino)methane in acetone at room temperature. The structures of **303** and **304** were confirmed by X-ray method. Both complexes exhibit bright red luminescence in solid state with  $\lambda_{em}$  = 638 nm (**303**) and 655 nm (**304**). Authors demonstrated that complex **304** easily transforms into binuclear Pt<sup>IV</sup> complex with composition [Pt<sub>2</sub>Me<sub>4</sub>(bzql)<sub>2</sub>( $\mu$ -I)<sub>2</sub>] under the action of

the excess of MeI in acetone at 0 °C during 1 h, the structure of obtained product was confirmed by X-ray data.

Novel cyclometallated Pt<sup>II</sup> complexes **306-308**, bearing the same (C^N) ligand, бензо[*h*]хинолин were synthesized, and impact of modification of an auxiliary ligand on phosphorescence efficiency in comparison with the earlier synthesized complex **305** was described.<sup>172</sup> The structure of compound **305** was confirmed by X-ray analysis,<sup>238</sup> it exhibits an intensive luminescence with  $\lambda_{em} = 550$  nm in hexane at room temperature. It was shown that the complex emits from metal-perturbed ligand-centered triplet state with a speed constant  $1.4 \cdot 10^5$  s<sup>-1</sup>.

#### Structures 305-308

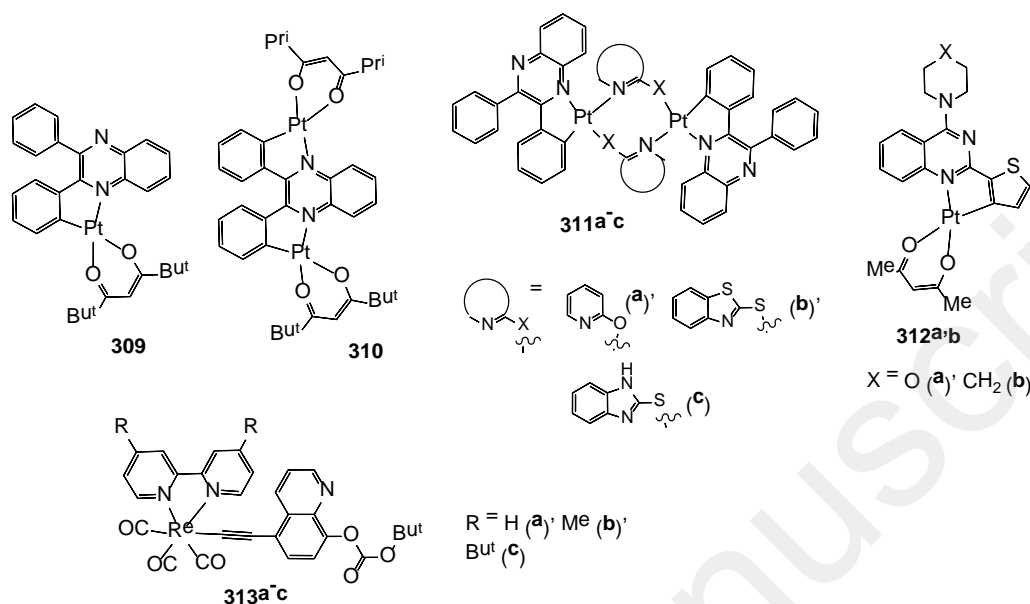


Authors performed calculations for structures **306-308** by means of DFT and TDDFT methods: geometry in the basic and the low-lying triplet excited state, frontal molecular orbitals, charge transfer, phosphorescence, speed constants of radiation and non-radiation processes.<sup>172</sup> The obtained results allowed to conclude that the replacement of dipivaloylmethane with other ligands in these structures led to the improvement of rigidity which can weaken non-emissive ways. Complex **307** showed the balanced electronic and hole conductivity that is important for OLED materials. Complexes **306** and **308** could be regarded as excellent phosphorescent materials for devices with high phosphorescence quantum efficiency.

2,3-Diphenylquinoxaline represents a convenient C^N-ligand for the synthesis of mono- and the binuclear cyclometallated Pt<sup>II</sup> complexes.<sup>239</sup> So, the reaction of this ligand with K<sub>2</sub>PtCl<sub>4</sub> (1.5 equiv) in acetic acid led to the mixture of dichlorinated mono- and binuclear intermediates, which under the action of dipivaloylmethane transformed into the mixture of mono- (**309**) and binuclear (**310**) complexes.<sup>237</sup> Products were separated by column chromatography and characterized by NMR <sup>1</sup>H and mass spectra data. Both complexes possess fluorescence in degassed DCM at room temperature with  $\lambda_{em} = 668$  nm ( $\Phi_F = 0.14$ ) (**309**) and  $\lambda_{em} = 749$  nm ( $\Phi_F = 0.025$ ) (**310**). At 77 K emission spectra are structured and exhibit maxima in red or near IR range at 625, 677, 747sh nm (**309**), 694, 760 nm (**310**). Authors noted that binuclear complexes on the basis of 2,3-

diphenylquinoxaline are potential phosphorescent materials which strongly absorb and brightly emit with extraordinary low energy.

### Structures 309-313



2,3-Diphenylquinoxaline was used for the synthesis of Pt<sup>II</sup> complexes **311a-c** with other structure.<sup>240</sup> The method includes the formation of dichloro-containing intermediate (2,3-Ph<sub>2</sub>quin)<sub>2</sub>Pt<sub>2</sub>Cl<sub>2</sub>, which interacts with auxiliary ligand (2-hydroxypyridine, 2-mercaptothiazole, 2-mercaptobenzimidazole) in THF in the presence of sodium hydride leading to complexes **311**. The structure of **311a** was confirmed by X-ray method. Complexes **311b,c** exhibit luminescence in DCM at 25 °C in red range c  $\lambda_{em} = 744$  nm and 745 nm correspondently. At 77 K the blue shift of emission band took place at 37 nm (**311b**) and 17 nm (**311c**). A larger shift was observed in the PMMA film (up to 665 nm and 626 nm respectively). Authors reported that emission spectra of complex **311a** could not be measured.

We synthesized complexes **312a,b** on the basis of 2-(thiophen-2-yl)-4-(morpholin-4-yl) and 2-(thiophen-2-yl)-4-(piperidin-1-yl)quinazolines as (C^N) ligands.<sup>241</sup> The structure of **312a** was confirmed by X-ray method. Both complexes exhibit orange luminescence in acetonitrile with emission maximum at 584 nm (**312a**) and 579 nm (**312b**).

Unlike to well-known Pt<sup>II</sup> complexes, exhibiting luminescent properties and widely presented in scientific literature, there are only few compounds of other d-element such as Re, tricarbonyl-diimine complexes of the last, containing azine or benzazine fragment with the formation of Re-C bond, also possess luminescence. So, in recent work<sup>242</sup> the new class of complexes Re<sup>I</sup> **313a-c** including 5-alkynyl-8-hydroxyquinoline derivative in the structure was presented. Compounds were obtained by the reaction of [Re(CO)<sub>3</sub>(bpy)Cl] with 8-*t*-butyloxycarbonyloxy-5-ethynylquinoline in THF in the presence of AgOTf and TEA under reflux

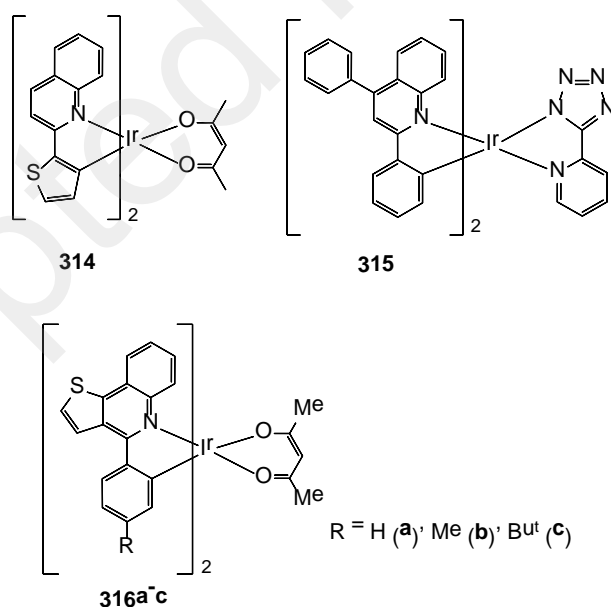
in nitrogen atmosphere in the dark during 24 h. Structures of compounds were determined by  $^1\text{H}$  NMR, IR and mass-spectra data as well as by X-ray data for the complex **313c**.

Complexes **313** demonstrated red luminescence in DCM, in emission spectra wide bands with maxima at 643–632 nm were observed; in solid state the bands were blue-shifted to 595–575 nm. Rather long luminescence lifetime measured at low and ambient temperature allows to assume the triplet nature of emission.

#### V.1.4. Complexes with $\text{Ir}^{\text{III}}$

Cyclometallated  $\text{Ir}^{\text{III}}$  complexes represent the most studied class of the compounds used for the creation of the phosphorescent materials emitting in red or near IR range that was outlined in recent reviews.<sup>211,243</sup> In work<sup>243</sup> a number of  $\text{Ir}^{\text{III}}$  complexes on the basis of 2-phenylquinoline and 2,4-diphenylquinoline were presented. 2-Thienylquinoline was used as one more C,N-ligand for the synthesis of the  $\text{Ir}^{\text{III}}$  complex (**314**), acetylacetone acts as an auxiliary ligand.<sup>244</sup> Compound exhibits red photoluminescence with  $\lambda_{\text{em}} = 629$  nm in DCM. Values of HOMO and LUMO levels and energy gap were calculated from the data of cyclic voltammetry. OLED fabricated on the basis of the complex **314** demonstrated clear red phosphorescence with narrow value of the complete width on a half of height (46 nm), the maximum brightness of 24,000  $\text{cd/m}^2$  and EQE = 11.1 %.

Structures 314-316



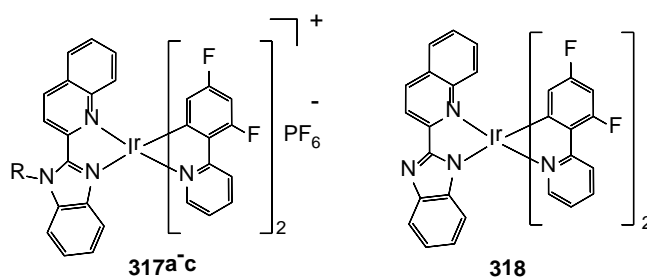
The incorporation of 2-(1H-tetrazol-5-yl)pyridine as an auxiliary ligand into iridium complex **315** based on 2,4-diphenylquinoline allowed to obtain new thermostable phosphorescent emitter.<sup>245</sup> Photophysical characteristics demonstrated the mixing of singlet and triplet excited states. This complex exhibits orange luminescence in DCM with  $\lambda_{\text{em}} = 578$  nm, quantum yield 0.87.

Phosphorescence lifetime at room temperature is 1.34  $\mu$ s. OLED fabricated with complex **315** as dopant-emitter possessed high efficiency, brightness and a yellow-orange emission.

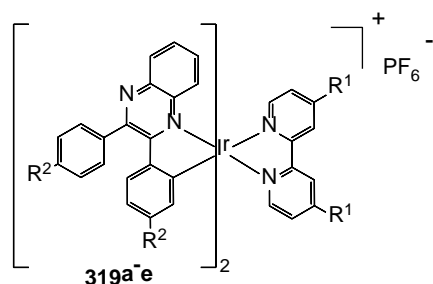
4-Arylthieno[3,2-*c*]quinoline was used as cyclometallating ligand with expanded  $\pi$ -conjugation system for the synthesis of Ir<sup>III</sup> complexes **316**.<sup>173</sup> The obtained complexes are thermostable (5% of weight loss was observed at a temperature more than 340 °C). All complexes demonstrated red luminescence in DCM solution ( $\lambda_{em}$  = 612–617 nm). Photoluminescence quantum yields for complexes **316** doped into 4,4'-*N,N'*-dicarbazolebiphenyl films at concentration of 4 weight % on air proved to be 0.46–0.47. The luminescence lifetime of compounds **316** measured in degassed DCM at ambient temperature is within 1.58–1.71  $\mu$ s that confirms their triplet-emitting nature. Red phosphorescent OLEDs were fabricated on the basis of these complexes, the device based on the complex **316a** demonstrated the best characteristics with EQE = 22.9%.

Quinoline containing benzimidazole at position 2 was used as an auxiliary N<sup>N</sup>-лиганд in the synthesis of Ir<sup>III</sup> complexes **317**, **318**.<sup>246</sup> The structure of compounds was confirmed by X-ray. It is shown that in complexes **317** the cyclometallated fragment [Ir(dfppy)<sub>2</sub>]<sup>+</sup> (dfppy is difluorophenylpyridine) is coordinated with neutral benzimidazole molecule, forming the cationic Ir<sup>III</sup> complex. In the compound **318**, the fragment [Ir(dfppy)<sub>2</sub>]<sup>+</sup> is coordinated with benzimidazole anion forming neutral Ir<sup>III</sup> complex. All complexes differ with their molecular packing. Both types of complexes exhibited luminescence in DCM at ambient temperature; while compounds **317a-c** demonstrated strong emission bands with  $\lambda_{em}$  = 558, 572 and 573 nm respectively and wide shoulder at 585 nm (**317a**), 600 nm (**317b,c**), complex **318** exhibited rather weak emission at 546 nm. The luminescence quantum yields in DCM are 0.14–0.18 (**317a-c**) and 0.032 (**318**). At 77 K all complexes demonstrated rigidochromism with the shift of emission bands to the short-wave range. In solid state at ambient temperature all complexes demonstrate intensive luminescence, compounds **317a-c** – yellow, complex **318** – orange with the red-shifted emission maxima in comparison with solutions, and the degree of shift is various for compounds **317** and **318**. Authors noted distinct influence of molecular structure of these complexes on their photophysical properties. It is interesting to note that complexes **317a** and **318**, which differ in nitrogen atom of imidazole cycle involved in the complexation, are able to switch the luminescence between the strong ( $\lambda_{em}$  = 558 nm) and weak ( $\lambda_{em}$  = 546 nm) luminescent state under addition of NEt<sub>3</sub>/TFA that is attributed to their structural interconversion.

### Structures 317-319



317: R = H (**a**), Me (**b**), n<sup>-</sup>C<sub>8</sub>H<sub>17</sub> (**c**)

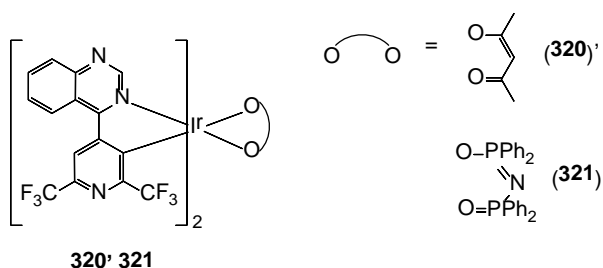


R<sup>1</sup> = H, R<sup>2</sup> = Me (**a**);  
R<sup>1</sup> = CONH<sup>-</sup>C<sub>8</sub>H<sub>17</sub> n, R<sup>2</sup> = H (**b**), Br (**c**), Me (**d**), OMe (**e**)

Substituted quinoxalines are also used as cyclometallating ligands in the synthesis of Ir<sup>III</sup> complexes, for example, for precise tuning of luminescent properties. So, in work<sup>247</sup> a number of Ir<sup>III</sup> complexes (**319a-e**), on the basis of the *p*-substituted 2,3-diphenylquinoxalines as (C^N) ligands and 2,2'-bipyridine or its 4,4'-dioctylamidoderivatives as an auxiliary ligands were synthesized. Structures of compounds are characterized by spectral data and X-ray for complexes **319a** and **319d**. These complexes demonstrated luminescence with emission maximum at 619–640 nm depending on the nature of substituents and solvent, quantum yields are low (0.018–0.027). On the basis of experimental and theoretical studies of complexes **319** authors came to the conclusion that the impact of <sup>3</sup>MLCT in excited state is significant, and mixing <sup>3</sup>MLCT/<sup>3</sup>LLCT in the most low-energy absorption and emission bands takes place.

As it was already mentioned, quinazoline derivatives are actively used as ligands for the synthesis of metal complexes including cyclometallated ones.<sup>23</sup> Incorporation into the position 4 of quinazoline of 2,6-bis(trifluoromethyl)pyridyl substituent, capable to affect on molecular packing and electronic mobility due to CF<sub>3</sub> groups, allowed to obtain Ir<sup>III</sup> complexes **320**, **321** demonstrating highly effective orange-red electroluminescence.<sup>248,249</sup> Compounds include different auxiliary ligands, they were characterized by spectral data, and the structure of complex **321** was confirmed by X-ray data. Thermal, electrochemical and photophysical properties of these compounds were studied.

**Structures 320, 321**



Both complexes possess strong phosphorescence in DCM solution with emission maximum at 588 nm and quantum yield 0.91 (**320**), 0.98 (**321**). Using these complexes as emitters, devices with one and two emitting layers (EML) were created. Comparison of their characteristics showed that for double-EML devices they were much better one-EML. Also the nature of auxiliary ligand, the replacement of acetylacetonate with tetraphenylimidodiphosphinate (complex **321**) has great influence on electroluminescent efficiency. Higher characteristics were obtained for double-EML devices based on emitter **321** with addition of  $\text{Eu}^{\text{III}}$  complex  $[\text{Eu}(\text{dbm})_3\text{phen}]$  as sensitizer: the maximum brightness is  $129466 \text{ cd m}^{-2}$ , maximum energy efficiency is  $62.96 \text{ cd A}^{-1}$ ,  $53.43 \text{ lm W}^{-1}$  and EQE 20.2%. The obtained results demonstrate that  $\text{Ir}^{\text{III}}$  complexes with quinazoline C^N ligand represent perspective orange-red phosphorescent materials for OLEDs.

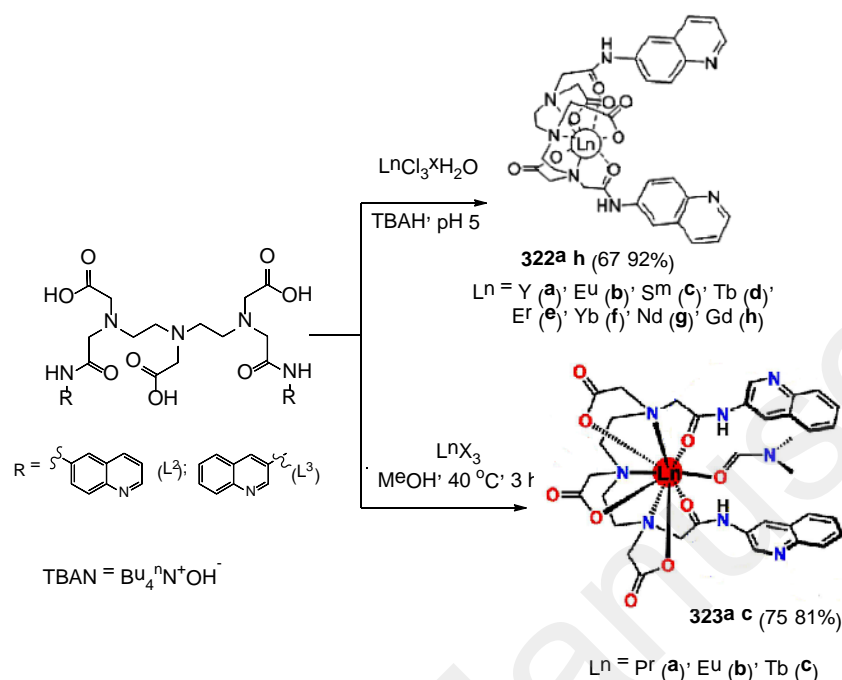
## V.2. Complexes with rare earth elements

Luminescent complexes of rare earths (REE) with organic ligands are well-known and found rather broad application due to excellent optical properties owing to the specificities of the electronic structure of these metals, to effective intramolecular energy transfer from ligand to metal atom (antenna effect), adjustable structure of complexes.<sup>9</sup> However REE complexes have also the drawbacks, related to low chemical, optical and thermal stability. For the improvement of properties of complexes research of new organic ligands continues.

Bisamides of diethylenetriamino- $N,N',N''$ -pentaacetic acid (DTPA), containing quinoline derivatives as amino component functioning as light harvesting fluorophore antenna, were used as polidentate ligands of  $\text{H}_3\text{L}^2$  and  $\text{H}_3\text{L}^3$  types for the synthesis of complexes with a number of  $\text{Ln}^{\text{III}}$  ions.<sup>250,251</sup> Complexes with composition  $\text{LnL}^2$  (**322a-h**) were obtained on the basis of ligands  $\text{H}_3\text{L}^2$  (Scheme 26) and it was shown that 6-aminoquinoline acts as a remote sensitizer for Ln-ions.<sup>250</sup> All compounds were characterized by mass spectra, and diamagnetic complex **322a** was studied by  $^1\text{H}$  NMR spectroscopy. The photophysical analysis of complexes showed that compounds Eu (**322b**) and Sm (**322c**) possess red emission, complexes Er, Yb, Nd (**322e-g**) emitted in near IR range (900–1500 nm) in powders and solutions. It should be noted that among compounds **322** the

complex Eu showed the considerable quantum yield (0.04) with emission in the visible range, and complex Yb demonstrated the most intensive emission in IR range in non-deuterated solvent.

**Scheme 26**

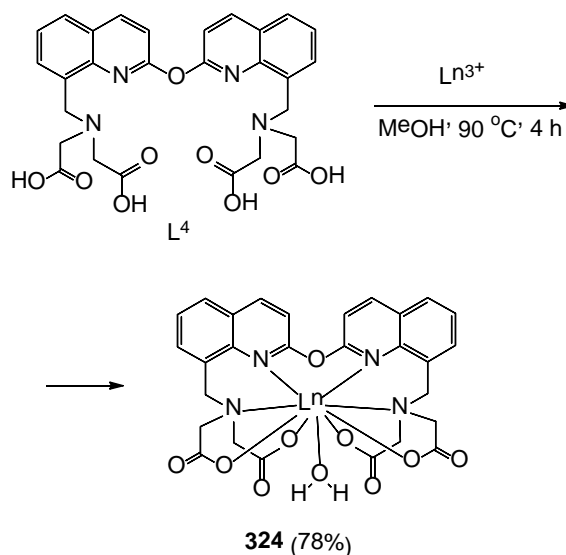


Lanthanide complexes **323** with ions of Pr (**a**), Eu (**b**), Tb (**c**) were synthesized on the basis of ligand  $\text{H}_3\text{L}^3$ .<sup>251</sup> The structures were confirmed by X-ray method, nine-coordinated geometry of  $\text{Ln}^{3+}$  ion ( $\text{LnN}_3\text{O}_6$ ) was revealed. Complexes  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  exhibit strong red and green emission in solvent under excitation with light at the absorption peak of quinoline chromophore. The experiments on DNA- and a protein binding, DNA-splitting and cytotoxic study showed that complexes **323b,c** have potential applications in biomedicine as the probing, therapeutic agents or potential transporters of chemotherapeutic drugs.

One more polydentate ligand containing quinoline fragments connected by O-bridge and carboxyl groups ( $\text{L}^4$ ) was synthesized and stable lanthanide complexes **324a,b** [ $\text{Ln} = \text{Eu (a)}, \text{Tb (b)}$ ] of structure  $\text{LnL}^4(\text{H}_2\text{O})$  were obtained on its basis in aqueous medium (Scheme 27).<sup>252</sup> The presence of water molecule in the coordination sphere was shown by mass-spectrometry method. Compounds exhibited red and green emission in water with rather high quantum yield: 0.095 for Eu of complex **324a** and 0.02 for Tb complex **324b**.

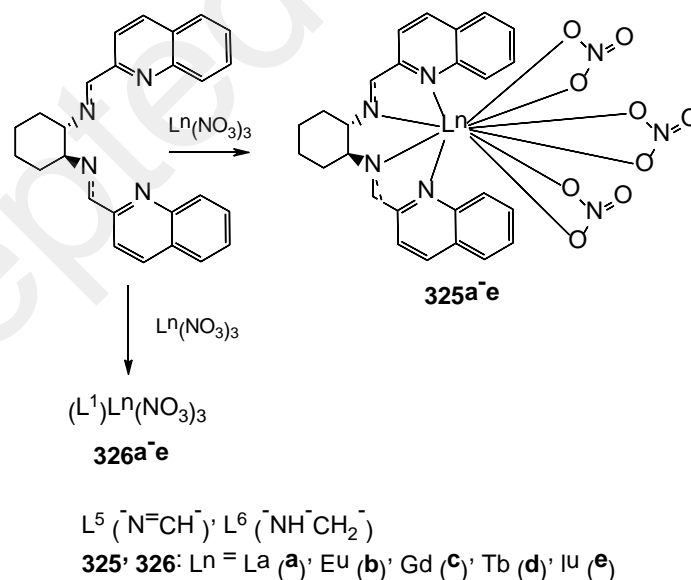
**Scheme 27**





Lanthanide complexes **325**, **326** with new chiral ligands containing two quinoline fragments connected with rigid 1,2-cyclohexandiamine fragment were synthesized (Scheme 28).<sup>253</sup> According to X-ray data, the composition of complex **325a** is  $(L^5)Ln(NO_3)_3$ , the similarity of X-ray diffractions in powder for all complexes allows to attribute such structure for all series. Reflection and emission spectra of compounds **325**, **326** at ambient temperature in powders were analysed and the possibility to obtain three different color emissions (blue, green and red) depending on the nature of chelated ion was shown. According to authors, the obtained complexes have potential application in the field of luminescent devices.

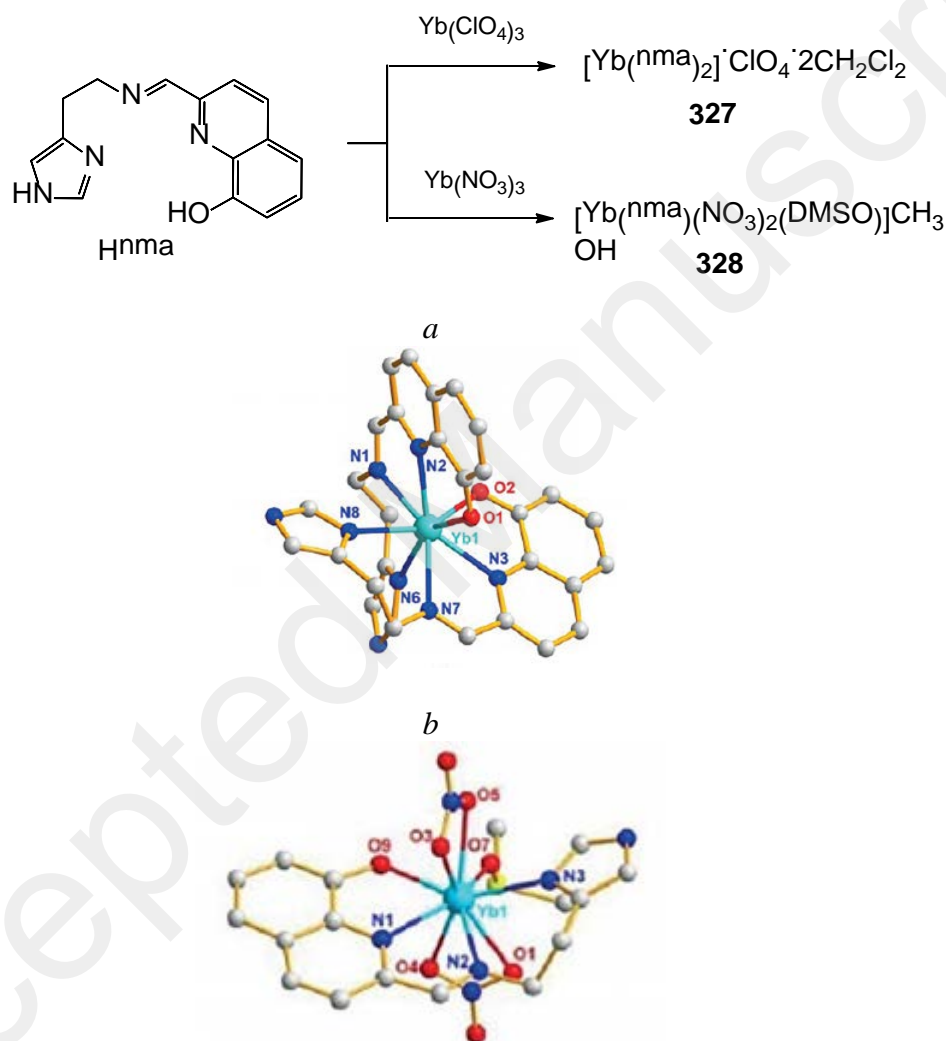
Scheme 28



Complexes **Yb 327**, **328** were obtained on the basis of N-(2-(8-hydroxyquinolinyl)methane(2-(4-imidazolyl)ethanamine) (Hnma) (Scheme 29).<sup>254</sup> It should be noted that ligand Hnma was formed *in situ* through the reaction of 8-hydroxyquinolin-2-aldehyde, histamine and ytterbium salt in the mixture MeOH/CH<sub>2</sub>Cl<sub>2</sub> in the case of perchlorate and

MeOH/CH<sub>2</sub>Cl<sub>2</sub>/DMSO in the case of nitrate. The structures of complexes were determined by X-ray method, it was shown that the anion plays an important role in the type of complexation. In the complex **327**, the Yb<sup>3+</sup> ion is completely encapsulated by two ligand molecules, and perchlorate anion is not coordinated, counterbalancing the positive charge, whereas in the complex **328** the Yb<sup>3+</sup> ion is coordinated by one ligand molecule as well as oxygen atoms nitrate anion and DMSO. The ligand nma works as antenna in complexes, activating luminescence in near IR range (900–1100 nm) with the bands characteristic for Yb<sup>3+</sup> (Figure 2).

Scheme 29



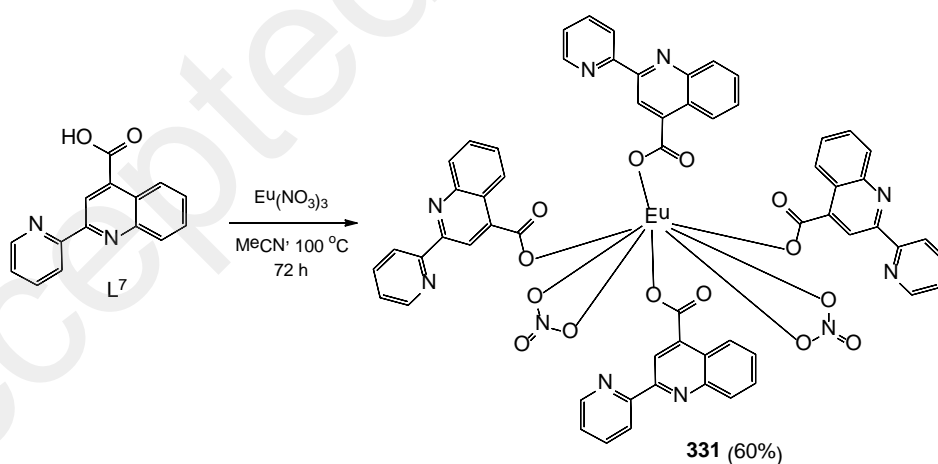
**Figure 2.** Molecular structure of complexes **327** (a), **328** (b).<sup>254</sup>

Complexes of some lanthanides with organic ligands continue to draw much attention also as single molecular magnets (SMM) demonstrating superparamagnetic behavior lower particular blocking temperature in molecular scale. Thus, new binuclear lanthanide complexes with composition [Ln<sub>2</sub>(dbm)<sub>4</sub>q<sub>2</sub>(MeOH)<sub>2</sub>] (**329**: Ln = Nd (**a**), Tb (**b**), Dy (**c**), Ho (**d**)) and [Er<sub>2</sub>(dbm)<sub>4</sub>q<sub>2</sub>(MeOH)]·MeCOMe (**330**)), containing 8-hydroxyquinoline (q) and dibenzoylmethane (dbm) ligands were synthesized.<sup>255</sup> The structures of compounds **329**, **330** were confirmed by X-ray

data; it was shown that  $\text{Ln}^{3+}$  ions are connected with  $\mu$ -phenol bridges of quinoline ligands. In complexes **329** each  $\text{Ln}^{3+}$  ion is coordinated with two bidentate dbm molecules, two q ligands and one MeOH molecule. Luminescent properties of obtained compounds were studied. Complex **329a** in solid state exhibits the typical emission of  $\text{Nd}^{3+}$  ion in near IR range with the most intensive band at 1060 nm. Magnetic properties of polycrystalline samples of complexes **329**, **330** in the temperature range 300–2 K were studied. The research of magnetism dynamics allowed revealing that complex **329c** (with  $\text{Dy}^{3+}$ ) demonstrated single molecular magnet behavior.

Coordination polymer **331** was synthesized by reaction of 2-(pyridin-2-yl)quinolin-4-carboxylic acid with europium nitrate in solvothermal conditions (Scheme 30).<sup>256</sup> The structure of polymer as confirmed by X-ray method; europium ion proved to be octacoordinated with four oxygen atoms from two nitrate ions and four oxygen atoms from four ligands. Each ligand is bidentate, as a result 1D structure forms. All nitrogen atoms are not coordinated. Polymer **331** exhibited luminescence typical for  $\text{Eu}^{3+}$  ion with emission bands at 592, 616, 652 and 696 nm, the most intensive was one at 616 nm. Under the action of HCl vapours on polymer the luminescence quenched more than for 90% during 120 sec. After the action of  $\text{NH}_3$  vapours the luminescence quickly returned (within ~90 sec). After 5 cycles polymer kept about 50% of luminescent intensity that testifies a possibility of its application as the sensor for fast visual detection of HCl. It was shown that protonation proceeds at pyridine nitrogen atom, changes energy of ligand excited state and makes it incapable to act as the antenna for  $\text{Eu}^{3+}$  ion.

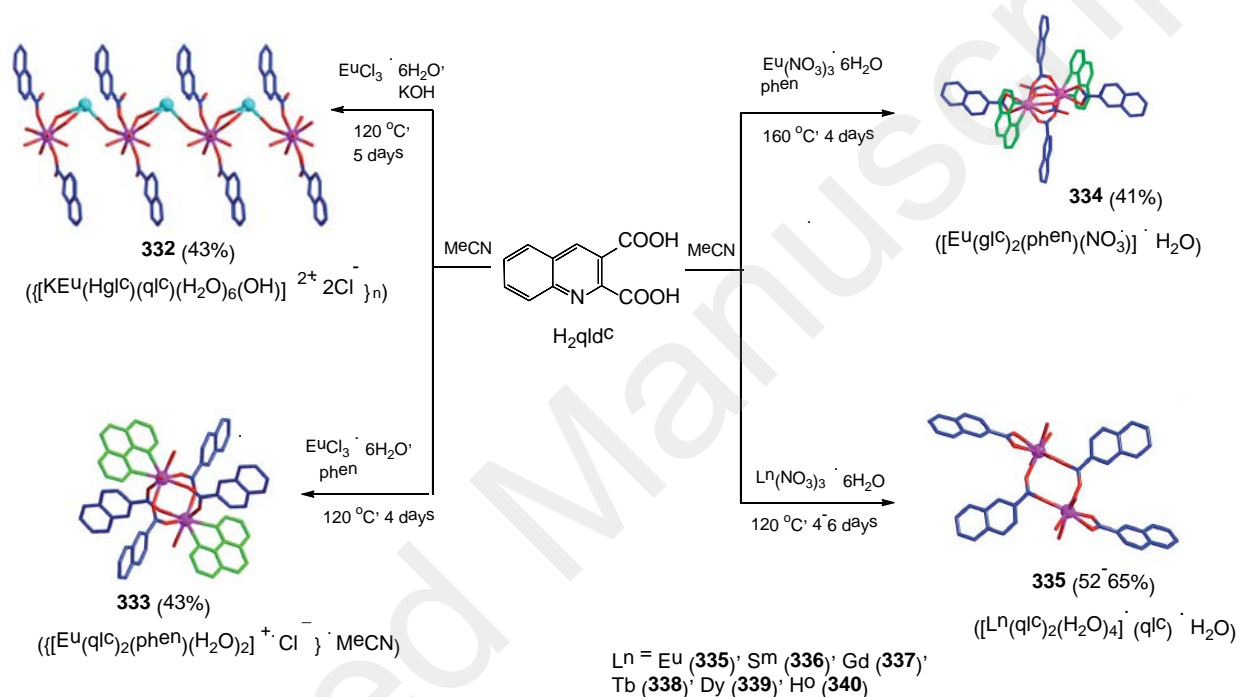
**Scheme 30**



The series of lanthanide complexes **332–340**, obtained on the basis of 2,3-quinolinedicarboxylic acid ( $\text{H}_2\text{glc}$ ) in solvo(hydro)thermal conditions was presented (Scheme 31).<sup>257</sup> As it was mentioned, this acid decarboxylizes into 3-Hglc under heating above  $120^\circ\text{C}$  and participates in the formation of complexes.<sup>221</sup> All complexes were characterized by IR spectra and X-ray diffraction in powders. In the structure **332**  $\text{K}^+$  ions act as structure-directing agents, implemented into the resulting crystal material. Incorporation of phenantroline (phen) led to the

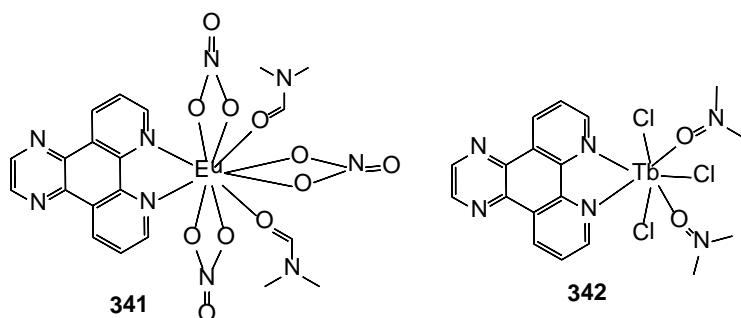
increase of system rigidity, dimer structures of complexes **333-335** are different, and complexes **335-340** are isostructural. Luminescent properties of all compounds were studied in solid state at 298 K or 77 K. Compounds **332-335** exhibit red emission typical for  $\text{Eu}^{3+}$  with the most intensive band at 613 nm. Complexes **333**, **334**, containing phen, possess higher values of luminescence lifetime than **332** due to sensibilisation not only HgIc, but also phen. Other complexes (**336-340**) exhibited luminescence typical for Ln ion. Hybrid materials, demonstrating strong red luminescence at concentration of 8%, were obtained by doping of complexes **333**, **334** in PMMA.

Scheme 31



Luminescent complexes of Eu and Tb (**341**), (**342**) were obtained on the basis of dipyridoquinoxaline (dpquin).<sup>177</sup> According to X-ray data, complexes are mononuclear. Eu ion is located in dodecaedric surroundment in the structure **341**, coordinated with nitrogen atoms of dpquin ligand, two DMF molecules and three  $\text{NO}_3^-$  anions. Tb complex has heptacoordinated structure of octahedric type; nitrogen atoms of dpquin ligand, two DMF molecules and three  $\text{Cl}^-$  anions participate in the coordination of metal. Both complexes are high emissive, dpquin ligand act as effective antenna; in emission spectra narrow intensive bands typical for Eu and Tb ions are observed. Authors showed prospects in application of these compounds for biomedicine.

### Structures 341, 342

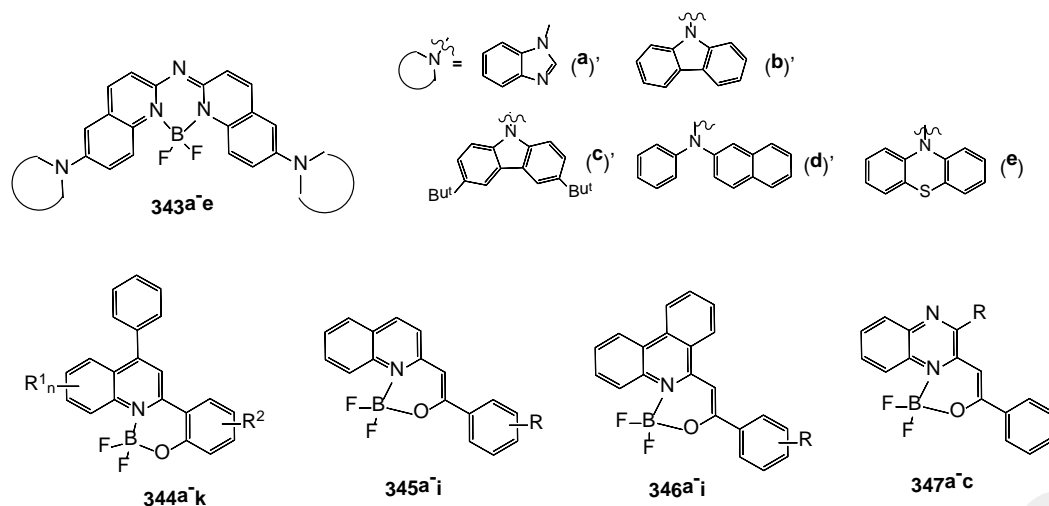


### V.3. Complexes with boron (III)

Tetracoordinated B<sup>III</sup> complexes with *N,N*- and *N,O*-heterocyclic ligands continue to draw much attention as bright emitting materials with a blue, green and orange luminescence. Some benzazines derivatives we reviewed<sup>253</sup> as such ligands.

The series of BF<sub>2</sub>-complexes **343a-e** was synthesized on the basis of bis(6-bromoquinolin-2-yl)amine as *N,N*-ligand with subsequent substitution of bromine with *N*-aryl residue.<sup>259</sup> All compounds were characterized by multinuclear spectroscopy, X-ray data were obtained for the complexes **343b,c,e**. Complexes **343** proved to be thermostable, they exhibit intensive luminescence in DCM solution and solid state in visible range. Depending on the nature of *N*-aryl substituent the emission maximum was observed at 440–505 nm, the quantum yield was rather high (0.24–0.78), complex **343b** possessing the highest quantum yield. The influence of protonation on luminescence of complex **343c** was studied and it was shown that both in solution and solid state (on filter paper) the luminescence changed from green to red and back at change pH from 1 to 12. The obtained results demonstrated that these complexes are able of emission tuning by protonation and could be regarded as good candidates for pH sensors, biological tests and OLED.

**Structures 343-347**



**344:** R<sup>2</sup> = H; R<sub>n</sub><sup>1</sup> = 7<sup>-</sup>Cl (a), 6<sup>-</sup>Cl (b), 6<sup>-</sup>F (c), 6<sup>-</sup>Br (d), 6<sup>-</sup>OMe (e), 6<sup>-</sup>Me (f), 6,7<sup>-</sup>Me<sub>2</sub> (g); R<sup>1</sup> = H; R<sup>2</sup> = H (h), 2<sup>-</sup>OMe (i), 2<sup>-</sup>OEt (j), 4<sup>-</sup>Br (k);  
**345, 346:** R = 4<sup>-</sup>NMe<sub>2</sub> (a), 4<sup>-</sup>OMe (b), 4<sup>-</sup>Me (c), 3<sup>-</sup>Me (d), H (e), 4<sup>-</sup>Br (f), 3<sup>-</sup>Br (g), 3<sup>-</sup>F (h), 4<sup>-</sup>CF<sub>3</sub> (i); **347:** R = H (a), Me (b), Ph (c)

Quinoline derivatives were used as *N,O*-ligands for the synthesis of BF<sub>2</sub>-complexes **344**, **345**.<sup>260-262</sup> Compounds **344** were synthesized on the basis of 2-(4-phenylquinolin-2-yl)phenols.<sup>260</sup> Incorporation of phenyl residue at the position 4 of quinoline could lead to the improvement of luminescent properties in solid state due to the decrease of  $\pi \dots \pi$ -interaction between chromophores. The structure of complexes was confirmed by <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B NMR, mass-spectrometry data and by X-ray for compound **344i**. All complexes exhibited luminescence in chloroform solution with emission maximum at 467–538 nm and large Stokes shift (up to 10231 cm<sup>-1</sup> for **344j**) and low quantum yield (0.03–0.12). Emission maxima of complexes in solid state are bathochromically shifted relative to solution (5–20 nm shift), luminescence is more intensive. Electrochemical properties of complexes were studied by CV method. Values of HOMO (-5.32–-6.10 eV) and LUMO (-2.64–-3.46 eV) energies as well as energetic gap (2.14–2.77 eV) were calculated, they were found to be close to values Alq<sub>3</sub> complex.<sup>260</sup> The obtained results demonstrate the existence an electron-transport properties of BF<sub>2</sub> complexes **344**.

Difluoroborates, obtained on the basis of 2-benzoylmethylenequinolines **345a-i**, were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, <sup>19</sup>F and <sup>11</sup>B NMR, X-ray diffraction, quantum chemistry, and X-ray analysis for compounds **345b-f,i**.<sup>261</sup> In solutions of these complexes through space spin-spin interaction constants (<sup>TS</sup>*J*) between <sup>19</sup>F and <sup>1</sup>H(8) or <sup>13</sup>C(8), nuclei were observed. The nature of bond in NBF<sub>2</sub>O fragment was studied, it was shown that B-N interaction is dative while bonds B-O and B-F are polar covalent. The clear dependence between the nature of the substituent R and the constant <sup>1</sup>*J*(<sup>11</sup>B, <sup>19</sup>F) was revealed. Complexes **345a-i** exhibit strong luminescence in chloroform with  $\lambda_{\text{em}}$  = 435–520 nm and quantum yield 0.37–0.94 depending on the nature of substituent.<sup>262</sup> The highest quantum yields were registered for compounds **345a,b** (0.86, 0.94) with electron donor substituent R, the largest bathochromic shift in absorption and emission spectra was observed for

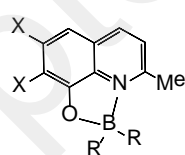
compound **345a** (with 4-NMe<sub>2</sub>). Authors demonstrated that absorption and emission spectra of such complexes can be well simulated by quantum chemistry methods.

In recent work,<sup>263</sup> BF<sub>2</sub>-complexes **346a-i** were obtained on the basis of phenacylphenantridine with the same substituents R as in compounds **345**. Phenantridine can be regarded as analog of benzoannelated quinoline or isoquinoline. Authors studied the effect of substituent and double benzoannellation on photophysical properties of complexes **346** in comparison with quinoline complexes **345** obtained earlier<sup>262</sup> by experimental and quantum methods. It was shown that the substituent R has the same impact, as in compounds **345**. Due to 4-NMe<sub>2</sub> groups present in **346a**, the considerable bathochromic shift in absorption and emission spectrum takes place that is due to charge transfer in excited state for this compound. Quinoid structure, arising in the course of this process, limits the mobility in excited state and explains high fluorescence quantum yield for complex **346a** (0.81). However, in general complexes **346** possess less intensive luminescence ( $\Phi_F$  for **346b-i** = 0.67–0.09) than analogs **345** ( $\Phi_F$  for **345b-i** = 0.94–0.37).

New quinoxaline- $\beta$ -ketoiminate boron difluoride complexes **347a-c** possessing tunable and fascinating photophysical properties ( $\lambda_{em}$  = 467–482 nm,  $\Phi_F$  = 0.78–0.92) have been developed.<sup>264</sup> Compounds **347** demonstrated unusual acidochromic behavior triggered by acid vapor.

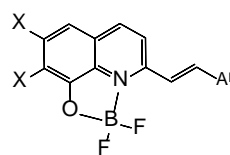
We synthesized BF<sub>2</sub> and BPh<sub>2</sub> complexes **348a-d**, **349a-d** with five-membered chelate cycle on the basis of 2-methyl-8-oxyquinoline and its 6,7-difluoroderivative.<sup>265</sup> Another ligand, 2-(2-hydroxyphenyl)-3H-quinazolin-4-one was used for the preparation of complexes **350a,b**, **351** with six-membered boron-containing cycle.

#### Structures 348-351



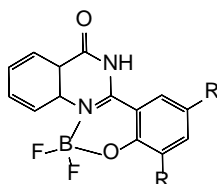
**348a-d**

R = Ph: X = H (**a**), F (**b**);  
R = F: X = H (**c**), F (**d**)



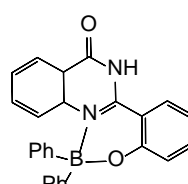
**349a-d**

R = Ph: X = H (**a**), F (**b**);  
R = F: X = H (**c**), F (**d**);  
Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>



**350a,b**

R = H (**a**), Bu<sup>t</sup> (**b**)



**351**

All complexes were characterized by NMR  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$  spectroscopy, mass-spectrometry data; X-ray analysis was performed for compound **349a**. Compounds exhibit luminescent properties with emission maximum at 390–502 nm and large Stokes shift, the colour and intensity are dependent on the nature of substituent both in ligand and boron atom. Thus, the presence of fluorine atoms in benzene ring of complexes **348** led to significant red shift of emission band and to increase in quantum yield from 0.005 to 0.025. Diphenylboron complexes **349a,b** exhibit higher quantum yield relative to difluoroboron ones (0.18 and 0.29 correspondently). The incorporation of *t*-butyl group into phenol fragment of compound **350b** led to long-wave shift of emission band and the increase  $\Phi_{\text{F}}$  from 0.09 to 0.36.<sup>265,266</sup> In the case of complexes with five-membered chelate cycle **348**, **349** the luminescence of diphenylboron derivatives (**348a,b**, **349a,b**) exceeds the luminescence of difluoroboron complexes (**348c,d**, **349c,d**).

## VI. Conclusion

During the last years there has been a growing interest to investigation of organic and organometallic push-pull chromophores for their further application in luminescent, photovoltaic and other optoelectronic devices. Indeed, in the context of “green” energy and reducing energy consumption, the development of new solar storage materials and the creation of energy-efficient lighting devices play a key role. In the field of new technologies, data storage and optical processing are important, and highly efficient materials with nonlinear optical properties are required. With respect to these applications, more preference is now given to organic and organometallic materials containing  $\pi$ -conjugated core than to inorganic materials due to lower cost, easier tunability and low toxicity.

In this context, the incorporation of benzazine fragments into the structure of benzazine fragments is interesting: as electron-deficient heterocycles, benzazines exhibit electron-acceptor character and can be used as acceptor part in push-pull structures, leading to ICT. Benzazine derivatives have a stronger electron-acceptor effect on the system than their pyridine and diazine counterparts. Benzazines can also be used as  $\pi$ -conjugated linkers. A lone electron pair of nitrogen atom can easily interact with a proton or metal cation, allowing for tuning of photophysical and electronic properties of target compound.

Analysis of the literature shows that various quinoline derivatives and their aza-analogs continue to attract attention as promising luminescent materials and components for optoelectronics. The review presents the main approaches to the synthesis and functionalization of  $\pi$ -conjugated benzazine chromophores. Traditional methodologies include the formation of benzazine ring using different condensation reactions. More modern methods consist in functionalization of already



formed benzazine core with application of Knoevenagel condensation and cross-coupling of different types from commercially available methyl- and halogen-substituted benzazines.

Many quinoline chromophores have found widespread use or appear promising. For example, ways of modifying structure **19** to provide a molecular switch and logic gates for processing information are discussed.<sup>267</sup> This review does not reveal any clear trends in the main uses of quinoline dyes. While for many quinoxaline chromophores, especially for 5,8-diarylquinoxaline derivatives, there is a clear trend – their design is implemented for photovoltaic devices as small molecules or polymers. The quinoxaline backbone is commonly used in systems such as the  $\pi$ -conjugated linker or the auxiliary electron acceptor group. Quinoxaline-containing polymers with different chiral side chains demonstrate a new class of materials with circularly polarized luminescence. According to our knowledge, such dyes are not yet used in industry; they are closest to commercial adoption from all the structures mentioned in this review. Another promising application of quinoxaline chromophores is related to nonlinear optical properties: recently interesting structures with 2<sup>nd</sup> order nonlinear optical properties, in which the quinoxaline fragment acts as  $\pi$ -conjugated linker or electron-acceptor part, have been obtained.

The development of quinazoline chromophores has started relatively recently, and so far a limited number of molecules have been developed, possibly due to the small amount of commercially available quinazoline-type reagents. However, recently such a promising direction for the application of these heterocycles, as the creation of pure organic chromophores for white OLEDs by partially protonating one of several nitrogen atoms of heterocyclic molecule and selecting a certain ratio of protonated to untonated forms of the benzazine derivative, has been proposed.

Annulation of benzazines with various fragments leads to new properties and applications. Dibenzo- and phenanthrolinequinazoline derivatives already find use as electron-transport, hole-transport layers, bis(indoloquinoxaliny) derivatives with various bridges represent promising emitters for phosphorescence OLEDs, derivatives of acenaphthoquinoxalinediimide are of interest as non-mullerene components for organic solar cells.

New properties of annelated benzazines were also revealed. The modification of quinoxaline with carbohelicene or tetrathiagelicene allowed the creation of non-planar molecular systems exhibiting circular-polarized luminescence (CPL). The V-shaped thiadiazole annelated quinoxaline molecules demonstrated an example of creating an emission system in a polar aqueous environment with double emission change. The novel T-shaped tetraphenylethylene substituted derivatives of acenaphthene- and phenanthrenquinoxaline showed aggregation-induced emission and mechanochromism as cyclomellating ligands with an extended  $\pi$ -conjugated system.

Much attention is paid to obtaining coordination compounds of benzazines with various metals: mono-, binuclear, cyclometallated, possessing dendrimer or polymer structure, exhibiting luminescent properties in a wide spectral range. Pure organic benzazine derivatives are used in promising directions associated with the design of fluorophores for controlled molecular photo switches; emitters exhibiting white emission; fluorophores with aggregation-induced emission in the red and near IR regions, which is important for biovisualization and biological research. Complexes of benzazines with such metals as Pt, Ir are already used or presented as promising high-performance phosphorescence emitters for OLED with tunable emission. Complexes of benzazine ligands with rare-earth elements possess unique chemical and photophysical properties, these structures are promising for biomedicine as probing and therapeutic agents. Compounds of lanthanides with functionalized benzazines also attracted attention as single-molecule magnets showing superparamagnetic behavior.

Despite the progress made in synthesizing and investigating functionalized benzazines, there are still challenges to be solved. One of them is related to the development of atom-economic and low-stage synthetic approaches using metal-non-catalyzed reactions, which will bring the processes closer to the basic principles of “green chemistry”, reduce the negative impact on the environment and economic costs.

Another problem is related to the design of highly rigid benzazine ligand structures to produce metal complexes capable of exhibiting the effect of thermally activated delayed fluorescence (TADF). In such compounds, the energy of both singlet and triplet excitons can be realized as emission through the singlet state, resulting in high quantum yields. TADF materials present an alternative to triplet emitters in OLEDs, which are characterized by low quantum phosphorescence yield.

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#### Data for front page

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Scientific interests: nucleophilic substitution of hydrogen, uncatalyzed by transition metal nucleophilic substitution of hydrogen in arenes and hetarenes, one-stage regioselective approaches to complicated heterocyclic structures, including bridged, alkaloid-like, supramolecular compounds; chemistry of fluorine-containing compounds, including heterocyclic ones; chemical aspects of environmental protection; biologically active compounds (antibacterial, antiviral, cardiotropic, antineoplastic agents).